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Sustainable Materials and Technologies 22 (2019) e00124

Contents lists available at ScienceDirect

Sustainable Materials and Technologies

journal homepage: www.elsevier.com/locate/susmat

Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery

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ARTICLE INFO

Article history:
Received 19 March 2019
Received in revised form 22 July 2019
Accepted 23 July 2019

Keywords:
Plastic waste
Circular economy
Thermochemical recycling
Feedstock recycling
Steam cracking
Gasification
Fluidised bed
Biomass

ABSTRACT

Plastics represent a serious waste-handling problem, with only 10% of the plastic waste (PW) generated worldwide being recycled. The remainder follows a linear economy model, involving disposal or incineration. Thermochemical recycling provides an opportunity to close the material cycle, and this work shows how this can be achieved using the existing petrochemical infrastructure. The transformation of a generic petrochemical cluster based on virgin fossil feedstocks into a cluster that is based on PW has the following proposed sequence: (1) the feedstock is partially replaced (45% on carbon basis) by PW; (2) the feedstock is totally replaced by PW; (3) the process undergoes electrification; and (4) oxy-combustion and carbon capture and storage are introduced to achieve 100% carbon recovery in the form of monomers or permanent storage. An alternative transformation pathway that includes the introduction of biomass is also considered. The energy and carbon balances of the proposed implementation steps are resolved, and cost estimates of the savings related to the feedstock and required investments are presented. The main conclusion drawn is that switching the feedstock from virgin fossil fuels to PW (Implementation steps 1 and 2) confers economic advantages. However, the subsequent transformation steps (Implementation steps 3 and 4) can only be justified if a value is assigned to the environmental benefits, e.g., CO_2 savings, increased share of biogenic carbon in plastic products, increasing recycling quotas, and/or the potential of the process to compensate for the intermittency of renewable power. It is also discussed how utilisation of the diverse compositions of PW streams by additional processes can meet the other demands of a chemical cluster.

1. Introduction

In relation to the United Nations' 17 sustainable goals, the current linear use of resources needs to be transformed to a circular form [1]. For the petrochemical industry, and especially that part of the industry that produces polymers, this entails reforming production systems and changing attitudes regarding the virgin fossil feedstock used. Plastics are technically advanced materials that provide the society with important products and services, i.e., medical devices and protective equipment save lives and packaging avoids food waste and transport emissions [2]. Plastics can be produced in vast quantities at a very low cost, making them affordable for all income levels. Accordingly, global production of plastics has steadily increased (by 11,000 kt/year) over the last decades, reaching a global production of 322,000 kt in Year 2015 [3].

Although the cost of plastic production is low because they are produced from fossil feedstocks, plastics account for only 4%–6% of the global consumption of fossil fuels. Thus, while plastics do not represent a vast drain on resources, they instead create a serious waste-handling problem. Due to their low value, plastics quickly become waste materials, which eventually end up in the environment. In fact, 302,000 kt of plastic waste were generated in Year 2015 [4], corresponding to 94% of the total production of plastic in the same year [3].

According to the IPCC waste hierarchy, waste should be first avoided and re-used, followed by recycling, energy recovery, and disposal. However, the overwhelming majority of plastic waste (PW) generated globally is currently disposed of, landfilled or simply lost to the environment. Geyer et al. [4] have estimated that 200,000 kt of plastics were discarded (i.e., neither recycled nor incinerated) in Year 2015, and the annual flow of plastic waste and litter into our oceans is estimated to be in the range of 4800–12,700 kt [5]. A portion of the dumped material consists of micro-plastics, which are the end-products of the breakdown

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https://doi.org/10.1016/j.susmat.2019.e00124

of meso-plastics and macro-plastics in beach environments and, to a lesser extent, originate from degradation in the marine environment [6] and from the run-off of "primary" micro-plastics, i.e., plastics manufactured in microscopic size.

The main reasons for the leakage of plastics into ecosystems are mismanagement and lack of waste collection systems, with large differences noted across countries, cities, and income level zones [7]. Waste collection and waste management represent a corner-stone in our society and are an integral part of the UN-designated sustainable goals. Good waste management systems not only make our cities healthy and sustainable (UN goal 11), but also ensure sustainable and efficient use of natural resources (UN goal 12) and preserve our oceans and seas (UN goal 14). However, two billion people have no access to waste collection, and improving the waste management infrastructure, while essential, will require time and substantial resources [8].

Due to lack of an economic driver for waste handling, large volumes of PW have been exported from the high-income to lower-income countries in East Asia and in the Pacific region for decades, with a heavy dependency on export to China. The global trade of PW in Year 2015 was 16,000 kt, of which 7300 kt were sent to China. The temporary Operation Green Fence introduced in Year 2013 reduced by 2000 kt the global trade in PW, and in Year 2018, China announced a new import policy that permanently banned the import of non-industrial PW. As a consequence, most of the 7300 kt of PW previously imported annually by China needs to find an alternative end-of-life solution. To date, the solution has been to send the PW to neighbouring countries, which do not have the capacity or resources to handle this waste, with consequences that are still unknown [9].

In Table 1, the most common polymers and their flows are listed, with polyolefins being the most common type of waste polymer. Polyolefins are used mainly in packaging, with short-life applications, being on average 6 months. Thus, almost all the produced packaging becomes waste in a rather short time. Polyolefins represent the largest single contributor to the PW total, with 141,000 kt in Year 2015, or 50% of the total PW [4]. In contrast, PVC has a longer life-time, as it is mostly produced and utilised for construction, which means that it is either accumulated in the stock or collected separately as part of construction and demolition site waste. In Europe, 40% of the produced PVC became waste in Year 2014, while the rest remained as plastic that was still in use [10]. Historically, the recycling of PVC has been troublesome due to its chlorine content, with the additional challenge of it being mixed in the packaging streams. However, since Year 2004, the share of PVC production used for packaging has decreased by half compared to the previous years.

The presence of contaminants and additives complicates the mechanical recycling of plastics, down-grading the produced products and/or requiring the use of virgin materials. On the one hand, contaminated PW requires intensive cleaning before recycling, which even with the latest technology entails the use of 2–3 m^3 of water per tonne of material [11]. On the other hand, additives are present in most plastics and constitute, on average, 7% of the global PW generated, mostly in the forms of plasticisers (34%), fillers (28%), and flame retardants (13%) [4]. For specific plastics, the share of plasticisers can be up to 70%, fillers 50%, and flame retardants 25% [12]. Calcium carbonate is among the most widely used fillers in the polymer industry, with the primary purpose of reducing the material cost, and, in some applications, improving the physical properties of the polymer [13]. In addition to the presence of contaminants and additives, the inherent properties of the polymer limit the number of times that products can be mechanically recycled. This means that even with the use of an advanced sorting system: mechanical recycling will only be affordable in very limited regions of the world, the traditional mechanical recycling of plastics will be limited, and the recycling will be associated with down-grading of the properties of the initial plastic material.

For instance, in a high-income country such as Sweden, where advanced collection and sorting systems already exist, 51% of the 1600 kt of PW handled in Year 2017 was in the form of unsorted streams, which are not suitable for mechanical recycling. Only 7.2% of the total PW was recycled into new products, 85.5% was incinerated with energy recovery, 0.35% was sent for deposition, and for 6.8% the final treatment could not be determined, of this material one part was exported and could not be further tracked [14]. Globally, only 14% of the PW generated was collected for recycling [4]. Overall, 2% of the PW generated was converted into products of similar quality, while 8% was recycled into low-value products and 4% was lost in the process [4,15]. This means that a minor fraction of PW is currently recycled, and that the existing recycling processes recover, on average, 70% of the carbon in the plastic stream with an energy efficiency of roughly 65%.

As a result, disposal and incineration remain the most widely applied waste-handling methods in the world, with roughly 60% of our PW being disposed of and 25% being incinerated [4]. Incineration is performed primarily to avoid disposal or to reduce the volume of PW that cannot be recycled mechanically, while heat, and in some cases electricity, are produced as by-products. In this process, the carbon that was sequestered in the plastic material is released as CO_2 to the atmosphere, and the heat is generated independently of the heat demand. This means that in many locations, incineration represents an inefficient use of the carbon in the waste fraction. It may also represent inefficient exploitation of the heating value of the waste when there is no corresponding demand for the produced heat. For instance, it is not uncommon that the heat produced in waste-fired plants is pumped into the sea in the summer-time due to insufficient demand.

The Swedish example shows that despite strenuous efforts in regards to collection and sorting, a substantial fraction of PW ends up as mixed waste that cannot be recycled mechanically. To avoid disposal and/or incineration, there is a need for efficient industrial processes that enable the recycling of mixed waste streams. One example of such a process is the Renescience technology, which is presently demonstrated at 120 kt/year scale in Northwich UK. Renescience eliminates the organic degradable fraction of the mixed waste in an enzymatic step and produces a bio-slurry that is subsequently fermented to produce methane [16]. The remaining fraction is separated mechanically based on density and using magnetic separation methods similar to those used

Table 1
Global generation of plastic waste in Year 2015 according to type of waste and industry [4]. Flows of plastic waste imported by China from the rest of the world [9].

Polymer type (data for Year 2015)	Global Primary Plastic Waste Generation Year 2015 (kt)	Imported to China Year 2015 (kt)	Main industry (% of polymer in industry/total for that polymer waste)
LDPE	57,000 (19%)	≈3600 (49%)	Packaging (>60%)
HDPE	40,000 (13%)		
Polypropylene (PP)	55,000 (18%)	n.a.	Packaging (40%)
Polystyrene (PS)	17,000 (6%)	≈100 (1%)	Packaging (40%), construction (40%)
Polyethylene terephthalate (PET)	32,000 (11%)	n.a.	Textiles (>60%) and packaging (<30%)
Polyvinyl chloride (PVC)	15,000 (5%)	≈300 (4%)	Building & construction (70%)
Others	69,000 (23%)	≈3400 (46%)	–
Additives	17,000 (6%)	–	–
Total	302,000	7300	–

LDPE, Low-density polyethylene; HDPE, high-density polyethylene; n.a., information not available.

by Stena Recycling (Halmstad, Sweden) after the shredding of automobiles and mixed metal waste collected from municipalities [17]. This approach facilitates the use of mixed plastic fractions but does not ensure the circular use of the materials.

Progression towards using plastic materials in a circular way requires a technology that treats any type of PW (sorted or unsorted) and produces plastics of the same quality as the original. This would close the material cycle, transitioning from flows directed according to the waste hierarchy (Fig. 1a) to circular use (Fig. 1b), i.e., the fraction that currently ends up in energy recovery or disposal becomes the feedstock for new plastics. This can be achieved by thermochemical recycling, which entails theoretically unlimited recycling of any plastic material (mixed or sorted), where the focus is on recovering the building blocks of the plastic materials. This solution can be applied in any part of the world regardless of the availabilities of advanced sorting systems, and, more importantly, it creates an economic driver for the collection and logistics of PW. Thermochemical recycling becomes an upgrading bridge between PW streams and a phase of new use. In fact, thermochemical recycling maximises the increase in value of the carbon atom in the PW, as compared to that obtained using any other existing recycling route, such as mechanical recycling, where the new use phase is ensured, albeit with a product of lower quality.

In thermochemical terms, three complementary recycling routes are conceivable, as depicted in Fig. 2, with an increasing thermodynamic penalty for Routes A, B and C, respectively. Route A is based on the direct recovery of monomers and valuable molecules from the original material through thermal cracking of the feedstock. This route corresponds to the traditional naphtha/alkane cracking process that is currently used for the production of monomers, mostly olefins. During cracking, part of the feedstock is inevitably converted into by-products that are not usable in the direct synthesis of plastics. If the goal is to achieve 100% carbon recovery, Route B and/or Route C must be applied in combination with Route A. Route B refers to the thermal decomposition of the material into syngas, followed by a synthesis process. This route involves steam reforming of hydrocarbons to CO and H_2, with adjustment of the H_2/CO ratio to suit the subsequent synthesis process. The synthesis can occur, for instance, via methanol if the final product is olefins. Route C refers to the combustion of the feedstock to cover part of the heat demand and to recover the carbon in the form of CO_2. Aiming for 100% carbon recovery, this CO_2 stream will be used as a carbon source for the synthesis, which requires balancing of the H_2 content of the syngas. Thus, H_2 will be produced by electrolysis of water, generating O_2 as a sub-product that can be used for oxy-combustion, i.e., combustion with near-pure oxygen whereby the temperature is regulated by recirculation of the flue gases.

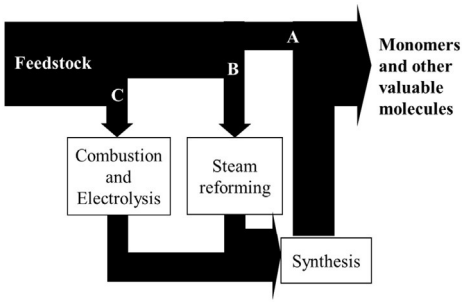

Fig. 2. Flows of carbon in the three thermal recycling routes for carbon recovery.

Route A is preferable from the thermodynamic point of view, as it preserves the structures of the existing molecules. However, the direct formation of valuable monomers is dependent upon the nature and composition of the feedstock applied, as shown in Table 2. In contrast, Routes B and C are less fuel-dependent and confer fuel flexibility upon the overall process.

The preferred pathway for conversion of recovered feedstocks to chemical building blocks can be evaluated based on the stoichiometry of the feedstock composition and the stoichiometries of the recycling routes shown in Fig. 2. To evaluate the potential of a feedstock to form different hydrocarbons, its elemental composition is considered. All feedstocks can be presented as a generic molecule normalized to its carbon content, $CH_iO_jN_kS_mCl_n$, and its apparent hydrogen-to carbon ratio (γ) can be calculated according to:

$$CH_iO_jN_kS_mCl_n \rightarrow CH_\gamma + H_2O + NH_3 + H_2S + HCl$$

As shown in the formula above, plastics based waste stream in the composition contain not only C, H and O but also impurities such as S, N and Cl. In the initial process of downgrading of the polymer chains to shorter hydrocarbon species this generates N, S and Cl-containing compounds in the product gas. Those compounds are expected in majority to be released in form of the NH_3 or HCN, H_2S and HCl in the reducing environment that prevails in the steam cracker/gasifier and to satisfy the requirements of the downstream processes, they need to be removed prior utilisation of the gas.

Depending on whether the γ-value is close to 2, 1 or 0, the stoichiometrically favourable outcomes of Routes A, B and C will differ. Potential feedstocks for thermal recycling are grouped in Table 3 according to their γ-values, while the stoichiometries of the reactions related to each recycling route and feedstock group are summarised in Table 4.

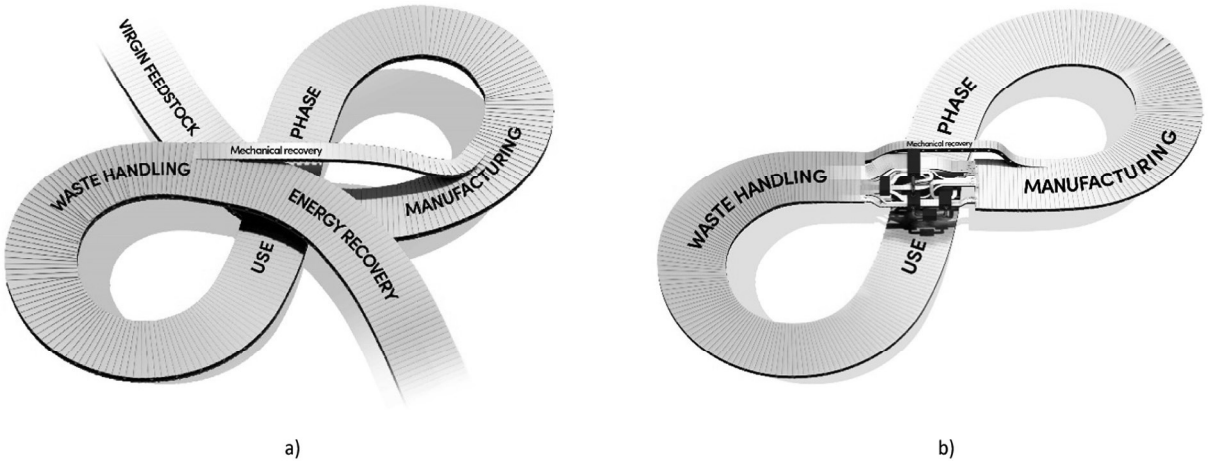

Fig. 1. Life cycles of plastic materials: (a) in the current socioeconomic system based on the waste hierarchy; and (b) in a system that has thermochemical recycling facilities.

Table 2
Typical compositions of the cracker gases derived from different feedstocks (ethane, propane, butane, naphtha [18]). The *Biomass* case corresponds to steam gasification of wood pellets in a fluidised bed of silica sand at 820 °C [19,20].

	Ethane	Propane	Butane	Naphtha	Biomass
γ (feedstock)	3.0	2.7	2.5	2.0	0.1
% weight (in the cracking products)					
Methane	4	23	20	17	9
H_2	4	2	1	1	3
Olefins	53	52	52	44	6
BTXS	1	3	4	15	3
Total others	38	20	22	24	79
Of which:					
Pyrolysis gasoline, fuel oil	1	2	3	10	0
CO	0	0	0	0	42
CO_2	0	0	0	0	33

BTXS, Benzene, toluene, xylenes, styrene; γ, apparent hydrogen-to carbon ratio.

In an extreme case, the feedstock of Group 2 includes the polyolefinic plastics (γ~2), which are the most abundant PW (recall Table 1) and are usually present in highly concentrated streams in countries with sorting systems. The feedstocks of Group 2 have stoichiometries similar to that of, for example, naphtha, which yields >40% olefins (Table 2). Therefore, they are expected to be suitable for direct recovery of olefins (Route A). Feedstocks with higher γ-values, such as ethane ($\gamma = 3$) can generate even higher yields of olefins, typically above 50% (wt.) [18,20]. At the opposite extreme, Group 0 and Group *Biomass* include predominantly oxygen-rich molecules, which have a biomass-like stoichiometry, here represented as $C{\cdot}{}^{2}/_{3}H_2O$. Due to their low apparent hydrogen-to carbon ratio (γ~0), Groups 0 and *Biomass* are best suited to the combustion route (Route C), where the feedstock is utilised to cover the heat demand of the process and to provide CO_2 for the subsequent synthesis. Note that when feedstocks with higher γ-values are processed via Route C, their hydrogen contents are lost in the form of water, which imposes a higher demand on the electrolyser (compare Reaction C2 for the different feedstock groups). If heat is not required, Groups 0 and *Biomass* can be treated instead via route B. The intermediate Group 1 (γ~1) can be processed via the different routes. The choice of route will depend on: whether the feedstock arrives in mixed or sorted form, the heat demand of the process, and whether the products of the thermal decomposition are the desired final products.

The decision as to whether to apply these routes rather than incineration relies heavily on the value of retaining the carbon of the feedstock within new products and the related cost for CO_2 emissions to the atmosphere. The current trend is towards phasing out the use of fossil-derived carbon, in combination with the promotion of renewable electricity production. A likely consequence of this transition is that the carbon molecule will become more valuable than electricity, in line with the regulatory framework derived from the Paris Agreement [21]. Thus, a major part of the heating of industrial processes that currently entails the burning of carbon-based fuels will gradually be replaced by electrical heating [22,23].

In a petrochemical cluster, a high cost for emitting CO_2 will have major consequences, as combustion is the main pathway for valorising the various side-streams that are not upgraded to products and for producing heat for the processes. This current strategy for the side-streams is in line with our traditional view that CO_2 can be deposited in the atmosphere for free. In a scenario of circular carbon usage, in which 100% carbon recovery is the ultimate goal, the heat generated from combustion will be replaced to the greatest extent possible by electric heating, while the CO_2 produced from combustion of any carbon-containing waste-stream should be recovered according to Route C, thereby using the carbon in a synthesis process (see Fig. 2). If that is not possible, the carbon could be stored in a geological site, preferably as CO_2.

Considering the UN goals for sustainability and the inherent nature of plastics, the feedstock for the production of these materials should be restricted to carbon that is already stored in plastic products and current wastes. This would impose a cap on the global use of newly extracted fossil fuels for the manufacture of plastics. Any extension of this cap or use of make-up material to compensate for unavoidable leakage, e.g., due to mainly natural degradation, should be off-set by biogenic carbon from dedicated biomass streams or by carbon extracted from the atmosphere through direct air capture.

In a scenario that is likely to be enforced by aggressive climate regulations and that will be dominated by renewable-based electricity, non-free CO_2 emissions, the phasing out of fossil fuels, and circular usage of materials, the introduction of biomass in a thermochemical recycling system (Fig. 2) offers multiple advantages. First, the extraction of virgin fossil feedstock related to the production of plastics would become unnecessary, as biomass could compensate for both the leakage of plastics to nature due to degradation and demand for plastic materials. Second, the combustion of biomass could complement electric heating and compensate for the fluctuations in the availability of renewable electricity. Third, by recovering the CO_2 produced during the combustion of biomass (Route C in Fig. 2), the share of biogenic carbon in the final plastic material would be increased. With the focus on carbon recovery in the overall process, waste wood would be used preferentially, thereby avoiding additional extraction of biomass from the ecosystem.

In summary, since we started to produce plastics in huge quantities (in the middle of the 1950s) up until Year 2015, we have produced >6 billion tonnes of plastics, approximately 79% of which is still present in our geosphere in products that have been deposited in landfills or dispersed in nature [4]. In the situation where there is not a further application, these plastics will accumulate in the geosphere due to their more or less un-degradable nature. Therefore, there is a need, but also an unexploited opportunity, to build a circular economy around plastic materials. To realise this potential, recycling processes that generate plastics with their original level of quality in technically and economically feasible manners are required. The focus of the present work is to explore the possibility to close the material cycle of plastic products, which today mostly follows a linear path.

In the present work, we present an outline and cost estimate for the transformation of an existing petrochemical cluster that uses naphtha/alkanes, together with natural gas as feedstocks, into a petrochemical cluster that is based on 100% recycled or renewable feedstocks, and with a carbon utilisation rate that is close to 100%. The solution presented in this work is based on the needs and the possible exploitation of the existing infrastructure of the petrochemical cluster in Stenungsund, Sweden. This solution exploits the experience gained from a first-of-its-kind 20-MW plant that uses forest biomass (fuel

Table 3
Grouping of recovered materials that can be used as feedstock for thermal recycling, and the most-suitable thermal recycling route according to their apparent hydrogen-to carbon ratios (γ-values).

Feedstock group	γ-value	Examples of feedstocks	Suitable recycling route
Group 2	~2	Polyolefinic plastics PE and PP	Route A
Group 1	~1	PVC, epoxy, nylon, ABS, polystyrene, polyurethane, polycarbonate	Route B/C/A
Group 0	~0	PET, carbon fibres, PMMA, synthetic textiles, e.g., viscose and polyester	Route C/B/A
Group *Biomass*	~0	Lignocellulosic materials, and natural textiles, e.g., cotton, wool, etc.	Route C/B

PE, polypropylene; PP, polypropylene; PVC, polyvinyl chloride; ABS, acrylonitrile butadiene styrene; PET, polyethylene terephthalate; PMMA. polymethyl methacrylate.

Table 4
Stoichiometries of the three thermal routes to recover olefins (CH_2) from a generic feedstock with different apparent hydrogen-to carbon ratios (γ-values). Route A: Direct formation of monomers and other products. Route B: Steam reforming and synthesis of olefins via methanol. Route C: Oxy-combustion with H_2 addition via electrolysis, followed by synthesis via methanol. The labels for the individual chemical reactions are indicated in the second column.

Route	Reaction	Feedstock Group 2 (γ-value ~2)	Feedstock Group 1 (γ-values ~1)	Feedstock Group 0 and Group *Biomass* (γ-values ~0)
A	A1	$(CH_2)_n \rightarrow n\,CH_2$	$(CH)_n \rightarrow n\,CH$	$(C \cdot 2/3H_2O)_n \rightarrow n\,(C + 2/3H_2O)$
	A2	$(CH_2)_n \rightarrow n(CH + 1/2H_2)$	$(CH)_n \rightarrow n(C + 1/2H_2)$	$(C \cdot 2/3H_2O)_n \rightarrow n\,(1/3CH_4 + 1/3CO_2 + 1/3C)$
	A3	$(CH_2)_n \rightarrow n\,(C + H_2)$	$(CH)_n \rightarrow n\,(1/2CH_2 + 1/2C)$	$(C \cdot 2/3H_2O)_n \rightarrow n\,(2/3CO + 2/3H2 + 1/3C)$
	A4	$(CH_2)_n \rightarrow n\,(1/2CH_4 + 1/2C)$	$(CH)_n \rightarrow n\,(1/4CH_4 + 3/4C)$	$(C \cdot 2/3H_2O)_n \rightarrow n\,(2/3CH_2 + 1/3CO_2)$
B	B1	$(CH_2)_n + nH_2O \rightarrow n(CO + 2H_2)$	$(CH)_n + nH_2O + 1/6nH_2O \rightarrow n(CO + 3/2H_2 + 1/6H_2O)$	$(C \cdot 2/3H_2O)_n \rightarrow n(CO + H_2 + 1/3O)$
	B2	$n(CO + 2H_2) \rightarrow n(CH_3OH)$	$n(CO + 3/2H_2 + 1/6H_2O) \rightarrow n(5/6CH_3OH + 1/6CO_2\,)$	$n(CO + H_2 + 1/3H_2O) \rightarrow n(2/3CH_3OH + 1/3CO_2)$
	B3	$n(CH_3OH) \rightarrow n(CH_2 + H_2O)$	$n(5/6CH_3OH + 1/6CO_2\,) \rightarrow n(5/6CH_2 + 1/6H_2O)$	$n(2/3CH_3OH + 1/3CO_2) \rightarrow n(2/3CH_2 + 2/3H_2O)$
C	C1	$(CH_2)_n + 3/2nO_2 \rightarrow n(CO_2 + 1/2H_2O)$	$(CH)_n + 5/4nO_2 \rightarrow n\,(CO_2 + 1/4H_2O)$	$(C \cdot 2/3H_2O)_n + nO_2 \rightarrow n(CO_2 + 2/3H_2O)$
	C2	$3H_2O \rightarrow 3H_2 + 3/2O_2$	$5/2H_2O \rightarrow 5/2H_2 + 5/4O_2$	$2H_2O \rightarrow 2H_2 + O_2$
	C3	$n(3H_2 + CO_2) \rightarrow nCH_3OH$	$n(5/2H_2 + CO_2) \rightarrow 5/6nCH_3OH + 1/6CO_2$	$n(2H_2 + CO_2) \rightarrow 2/3nCH_3OH + 1/3CO_2$
	C4	$nCH_3OH \rightarrow n(CH_2 + H_2O)$	$5/6nCH_3OH + 1/6CO_2 \rightarrow n(5/6CH_2 + 5/6H_2O)$	$2/3nCH_3OH + 1/3CO_2 \rightarrow n(2/3CH_2 + 2/3H_2O)$

demand of 6 t of dry biomass per hour [24], which on an energy basis corresponds to 3 t of naphtha per hour) to produce biomethane via gasification, as well as the knowledge acquired from dedicated, initial, pilot-scale experiments in the Chalmers 12-MW_{th} dual fluidised bed (DFB) system.

The aim of this work is to describe the technical and economic feasibilities of achieving close to 100% carbon recovery through the recycling of PW within the existing petrochemical infrastructure. In addition, we discuss its gradual implementation, potential thermal recycling routes, process flexibility, and the introduction of renewable feedstocks that act as make-up feedstocks and facilitate coping with growth of the market. The solution proposed herein is intended to: (i) be decoupled from any new extraction of carbon-containing resources (fossil or biogenic); (ii) compensate for the leakage of fossil carbon to nature by the introduction of residual streams of biogenic carbon; (iii) fulfil the energy demand of the process without generating or even accomplishing a net reduction of CO_2 emissions to the atmosphere; and (iv) be capable of taking up the carbon (as waste or CO_2) that has already been deposited in the environment, e.g., PW that is contaminating seas. It is assumed that this type of thermal recycling process for PWs will be introduced gradually at an existing site, resulting in minimal disruption of production and ensuring that the investment is spread out so as to go hand-in-hand with the development of regulations and markets.

2. Theoretical background

2.1. Thermal decomposition of plastics in a fluidised bed

In the thermal cracking of naphtha/alkane, the process is optimised to maximum the yield of olefins, which is achieved with high temperatures (in the range of 750–900 °C), high heating rates, short residence times (range, 0.08–0.25 s), and low partial pressures of the hydrocarbons (range, 0.2–1.0 kg steam/kg hydrocarbon, depending on the type of feed) [20]. The combination of these operating conditions is usually referred to as 'process severity' in the cracking literature, whereby higher severity corresponds to higher temperature and longer residence time. Similar yields of olefins may be achieved at higher temperatures and with shorter residence times, and vice versa. The partial pressure of hydrocarbons is adjusted by feeding a diluent inert gas, in this case steam, which means that the conversion of hydrocarbons occurs in a steam environment. Despite efforts to achieve optimisation, commercial crackers usually yield 40%–60% of hydrocarbons other than olefins, e.g., 4%–25% CH_4 and up to 10% benzene, depending on the feed and its H/C ratio, as shown in Table 2.

Similarly, for each plastic feed, the operating conditions (i.e., severity of operation) can be optimised for the formation of monomers and other desired molecules from the plastic feed, as intended in recycling Route A. The structure of the polymer determines the products that can be obtained by dictating preferred cleavage sites in the polymeric chain [39]. Fig. 3 presents a generic scheme for the products obtained from the thermal decomposition of a typical Group 2 (γ-value ~2) polyolefinic plastic and a plastic of Group 1 (γ-value ~1) that contains a large substituent group.

For the Group 2 polymers, polyethylene (PE) and polypropylene (PP), the scission of the polymer typically occurs at random locations at low temperature, and it results in a mixture of molecules of different lengths, whereas, at higher temperatures (e.g., 700–800 °C), the chain can also break at the edges (end-chain scission) to generate shorter molecules, such as methane [39,40]. At higher process severity, monocyclic aromatics are formed from the light olefins (e.g., via Diels-Alder reactions), which can grow into polycyclic aromatic hydrocarbons (PAHs) [41]. For polymers with large substituents along the main chain, such as polymethyl methacrylate (PMMA) of Group 0 and polystyrene (PS) of Group 1, monomers are usually formed at high levels at relatively low temperatures (i.e., 450 °C), e.g., 98% for PMMA and 75% for PS [42]. In the presence of oxygen-containing molecules in the cracker, such as steam and oxygen from the polymer molecule, carbon oxides (CO, CO_2) and hydrogen can also be generated via steam reforming and gasification. These reactions are promoted at higher process severity, and/or with the assistance of catalysts.

A reactor for cracking of plastic wastes should enable operating conditions similar to those applied in traditional crackers (temperature, heating rate, residence time), while being able to handle feedstocks that have high boiling points, carbon deposits, and inorganics. In these regards, the thermal cracking technology, which has been applied for >50 years and is based on cracking coils hosted inside a furnace, poses multiple challenges. Carbon deposition on the walls of the coils hinders heat transfer and increases the pressure drop along the coils [20]; while the construction material of the coils is damaged by corrosive ash elements [43], carburisation and/or erosion due to entrained solids [44]. In addition, clogging of the coils occurs if there is a high content of inorganic compounds, as can be expected in some plastic-containing waste-streams (e.g., up to 40% in automotive shredder residue, ASR [28]).

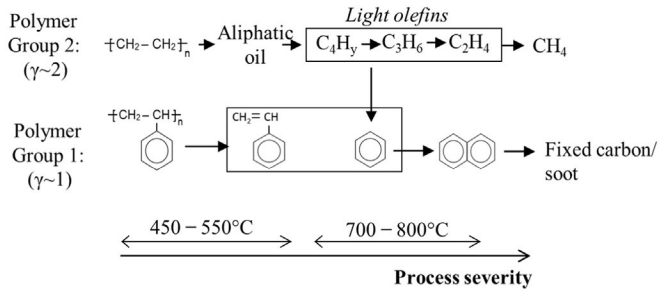

Fig. 3. Simplified schematic of product selectivity in relation to process severity for a polymer of Group 2 (γ~2) and a polymer of Group 1 (γ~1). The benzene and naphthalene rings represent monocyclic and polycyclic aromatic compounds, respectively. The γ-value refers to the hydrogen-to carbon ratio of the polymer.

In the past, pyrolysis and gasification of plastics were investigated in different reactor set-ups, and the fluidized bed technology has shown to be a suitable system for plastic recycling via pyrolysis and gasification [42,45]. Therefore, the fluidised bed reactor is here considered for the thermal cracking of plastic wastes due to: (i) its suitability to treat inhomogeneous solid feeds, the high heating rates achieved; (ii) the possibility to handle high ash contents; and (iv) the ease with which catalysts and sorbents can be introduced in the form of bed material. More precisely, in this work, the Dual Fluidised Bed (DFB) concept is applied, which conveniently separates the heat generation section (combustion) from the cracking section, similar to the approach used in a traditional tubular cracker. Compared with a single fluidised bed reactor, the DFB configuration has the additional advantages of diluting the cracking products only with steam (and not with flue gases) and regeneration of the catalyst from the carbon deposits in the separate combustion section.

DFB systems have been applied commercially for gaseous feedstocks since the 1940s, e.g., Fluid Catalytic Cracking (FCC) [46], where two circulating fluidised bed (CFB) reactors are inter-connected. Large-scale DFB plants for the treatment of solid feedstocks remain scarce, and they process mainly biomass or coal. Some examples of the DFB gasifiers are those in: Senden (HGA-Senden; 16-MW biomass) [47] and Gothenburg (GoBiGas, 32-MW biomass) [24], which are up-scaled versions of the 8-MW unit in Güssing, Austria [48]; and the TIGAR gasifier (15-MW lignite) operated by the IHI Corporation of Yokohama, Japan using their own design [49]. These examples consist of a CFB connected to a bubbling fluidised bed (BFB). The experience with plastic feedstocks at the MW scale in DFB gasification and pyrolysis units is even more limited; for example, AkzoNobel tested pyrolysis of mixed PW in the 1990s [27]. The technology was developed by Battelle for biomass gasification, and it was similar to that applied today in FCC.

Table 5 summarises the reported experiences with DFB systems and with 100% plastic as feedstock, as well as those with a single fluidised bed reactor and steam as the fluidising agent, since they are also representative of the gas environment of the cracking section of a DFB. For further information on the pyrolysis of plastics in a fluidised bed with N_2, the reader is referred elsewhere [50–52], and for air gasification to [53]; a more comprehensive overview of gasification of plastic waste

Table 5
Reported investigations of pyrolysis/gasification of plastics in fluidised bed and steam environments.

Reactor type (size)	Reference	Target product	Bed material	Operating conditions (temperature, fluidisation agent, residence time)	Plastic type
DFB pilot plant (100-kW, 7.5–13.6 kg/h)	[25]	Monomer recovery	Olivine	850 °C Steam (1.8–2.3 kg/kgC)	PE PP 20% PE, 80% PET 40% PE, 60% PS 50% PE, 50% PP
	[26]	Syngas	Calcite	807 °C Steam (2.1 kg/kgC)	Shredder Light Fraction (SLF)
DFB (200–400 kg/h)	[27]	HCl and fuel gas	Silica sand	700–900 °C	Mixed PVC-containing waste
DFB semi-industrial plant (2-MW, 370 kg/h)	[28] and in this work	Monomer recovery	Olivine	775–820 °C Steam (1.8 kg/kgC)	Automotive Shredder Residue (ASR)
	(this work)	Monomer recovery	Olivine	655–780 °C Steam (2.1 kg/kgC)	PE
Lab reactor-BFB (1–3 kg/h, D = 154 mm)	[29]	Olefins	Silica sand	600–800 °C 1.8–3.2 s (700 °C) Steam (1.8–3.0 kg/kgC)	95% PE/PP, 3% PS, 0.13% PVC
	[30]	1,3-butadiene, styrene, carbon black	Silica sand	500 °C 2.9 s N_2 or steam (2.7 kg/kgC)	SBR rubber
	[31]	Monomer recovery	Silica sand	600–700 °C 1.9–3.5 s N_2, pyrogas or steam (1.3–3.6 kg/kgC)	Rubber tires Hand gloves
	[32]	Olefins	Silica sand	545–750 °C 2.3–3.6 s Steam (1.0–3.5 kg/kgC)	Plastic packaging Bottles and boxes
	[33]	Olefins	Silica sand	600–800 °C Steam (0.6–3.1 kg/kgC)	HDPE
Lab reactor-BFB (0.1 kg/h, D = 51 mm)	[34]	Feedstock recovery	Hard burnt lime Quartz sand	600–700 °C 2.0–2.2 s N_2 or Steam (2.3–6.6 kg/kgC)	PP
Lab reactor- Conical Spouted bed pyrolysis (<0.3 kg/h, D = 12–60 mm),	[35]	Syngas	Silica sand Olivine Al_2O_3	800–900 °C Steam (1.2–2.4 kg/kgC)	20% PE, 80% PET
(followed by a BFB steam reformer)	[36]	H_2	Pyrolysis: Silica sand Reformer: Nickel-silica sand mixture	Pyrolysis: 500 °C Steam (3.5–5.9 kg/kgC) Reformer: 600–700 °C	40% PE, 60% PS
Lab reactor- BFB pyrolysis (0.06 kg/h, D = 25 mm), followed by a BFB steam reformer	[37]	H_2	Pyrolysis: Silica sand Reformer: Nickel	Pyrolysis: 600–700 °C Steam (3.5–4.7 kg/kgC) Reformer: 850 °C	50% PE, 50% PP
Lab reactor- BFB gasifier (0.02 kg/h, D = 30–60 mm) followed by a moving bed reformer	[38]	H_2	Gasifier: Silica sand Reformer: $NiO/NiAl_2O_4$ mixed with CaO	Gasifier: 820–880 °C Steam/N_2 (1.4–2.8 kg/kgC) Reformer: 810–880 °C	PE

using other types of reactors can be found in the recent review of Lopez et al. [54]. Pilot-plant trials and demonstration efforts with thermal gasification/pyrolysis of plastic wastes are reviewed in the next section (Section 2.2), while the focus in this section is on the gas composition and its dependence on operating conditions.

Several of the investigations listed in Table 5 have striven to identify the optimal conditions for monomer recovery, where PE has been among the most investigated of the plastics. Simon et al. [29] reported on the relationship between the product selectivity obtained from decomposition of the plastic and the temperature and gas residence time applied. At 600 °C, aliphatic oil was the dominant product, whereas in the temperature range of 650–750 °C, the aliphatic oil yield was insignificant, the highest gas yield was obtained, and the formation of monocyclic aromatics (e.g., benzene, toluene and xylenes; BTX) started to increase. At 800 °C, the gas yield declined due to the higher level of aromatisation of light olefins into aromatics, and methane production was at the highest level. Varying the gas residence time in the range of 1.8–3.2 s (at 700 °C) had only a slight effect on the product distribution. Similar trends were noted by Kaminsky et al. [33], with the difference that they had higher yields of styrene in their experiments owing to the higher content of PS in their feedstock. Typically, a peak in the production of olefins is observed, although the temperature at which this peak occurs differs for each polymer and the specific operating conditions, such as residence time and the use of catalysts, e.g., at 700 °C for olefins and at 750 °C for ethylene when pyrolysis mixtures of PE/PP/PS are used [29], at 700 °C during the pyrolysis of PE [33], and at 640 °C for the pyrolysis of PP [25].

The introduction of catalytic bed materials into the fluidised bed reactors has also been tested in previous investigations, with the objective of promoting steam reforming of the pyrolysis product. The catalysts have been tested either in the pyrolysis step [25,34,35] or in a secondary step of steam reforming of the pyrolysis products [36–38]. In the work of Wilk et al. [25], PE, PP, and plastic mixtures were gasified at 850 °C in a DFB system using olivine as the catalytic bed material. When the feedstock contained only PE, about 22 wt% of PE was recovered in the form of ethylene. High concentrations of methane were recorded, being almost double the concentration of ethylene (30 vol% versus 15 vol%). CO and CO_2 accounted for 15 vol% of the total product gas, which indicates the occurrence of steam reforming and gasification reactions. These results indicate that the degree of process severity was beyond that needed to maximise the yield of ethylene.

2.2. Pilot plants and trials of pyrolysis/gasification of plastics in fluidised beds

Producing plastics or petrochemicals in an economically viable fashion at a magnitude that is comparable to or even greater than is feasible with the existing infrastructure requires the construction of large-scale waste-recycling plants. Although PW gasification or pyrolysis has not yet been conducted at scales comparable to those of existing petrochemical clusters, some technologies have been demonstrated at relatively large scales. Most large-scale plants used for thermochemical conversion of PWs have been designed for energy recovery and many employ a two-step process, usually starting with low-temperature pyrolysis in a rotary kiln or drum, followed by heat recovery in a boiler. Examples of this are the pyrolysis process used by Babcock Krauss-Maffei Industrieanlagen GmbH (Munich, Germany), the PKA process, the EDDITh process carried out by Thide Environnement S.A. (Voisins-Le-Bretonneux, France) and l'Institut Français du Pétrole (IFP, Rueil-Malmaison, France), which has been operated at a capacity of 50 kt/year, and the Contherm process, which has been operated at 100 kt/year [55]. Many of these energy recovery processes have been reviewed by Malkow [55]. The Ebara TwinRec technology, which combines fluidised bed gasification with a combination of combustion and ash-melting [53,56], is operated at numerous plants in Japan at relatively large scale. For instance, the Kawaguchi plant, which was built in Year 2000, has been operated with municipal solid waste (MSW) at a capacity of 420 t/day [57].

There are also examples of industrial-scale plants for fuel or syngas production. For instance, the TEXACO process [27] has been demonstrated at a scale of 150 t of mixed plastic waste per day, generating 350,000 Nm^3 of syngas. The technology is based on the liquefaction of pre-shredded waste, followed by gasification of the heavy oil in an entrained-flow gasifier, operated at 1200–1500 °C with a mixture of oxygen and steam as the gasification agent. Side-products of this process include pure sulphur, ammonium chloride, vitrified slag, and fines. Large-scale gasification for the production of syngas, methanol, and electricity was carried out until Year 2010 in the SVZ Sekundärrohstoff-Verwertungszentrum Schwarze Pumpe GmbH (Spreetal, Germany) plant [58]. There, the core unit for solid waste gasification was based on seven fixed-bed gasifiers operating at 24 bar with a mixture of steam and oxygen as the gasification agent. Pre-treatment of the wastes, including crushing, removal of iron and metals, drying, and pelletisation, was required. Liquid wastes, including tar from the fixed-bed gasifiers, were gasified in entrained flow gasifiers. A British Gas/Lurgi slagging gasifier has been used to convert large fuel particles, while simultaneously vitrifying inorganic compounds. In the Enerkem Alberta Biofuels plant in Edmonton (Canada), over 100,000 t/year of non-recyclable and non-compostable MSW are processed via fluidised bed gasification and synthesis to produce annually 38,000 Nm^3 of ethanol and methanol [59].

The above-mentioned processes demonstrate the potential of technologies for syngas production or energy recovery based on PW. If the goal is the direct production of olefins or valuable molecules for new plastic synthesis, as is the case in the present work, either a two-step process that produces an intermediate oil or wax fraction by pyrolysis with subsequent treatment in a cracking reactor or direct cracking is required. Direct cracking to yield olefins is advantageous if integration with the gas separation unit and utilisation of a chemical cluster are possibilities. For remote and smaller-sized plants, pyrolysis is the preferred option, as separating and transporting the gas streams is not economically feasible. In this case, the light gases are combusted for heat production and a high yield of oil is in focus, while 100% carbon recovery becomes difficult.

In this context, fluidised bed reactors present several advantages, notably with regard to scalability, feedstock flexibility, and the possibility to re-generate the heat transfer surface, i.e., the bed material. Research on fluidised bed pyrolysis of PWs for fuel production was pioneered by Professors Sinn and Kaminsky, who developed the Hamburg fluidised bed pyrolysis process at the University of Hamburg. This process is presented in detail elsewhere [45], and some features of the process and obtained results are described here. Two pilot plants were put into operation, one with a capacity of 10–30 kg/h, and the other with a capacity of 1.5–2.5 t/day. The latter plant was designed for the recycling of tyres and could accommodate the direct feeding of whole tyres without prior size reduction. The pyrolysis was carried out at a high temperature (in the range of 700–800 °C), with nitrogen, steam or non-condensable pyrolysis gases as the fluidisation medium. Pyrolysis with steam was shown to produce high levels of olefins, at yields that were even higher than those obtained from naphtha/alkane crackers. Pyrolysis of PW that contained 1.2%wt PVC could be carried out without the detection of chlorine in the gas, as limestone was fed to the bed to neutralise the Cl by driving the formation of $CaCl_2$. Low levels of chloro-organic elements were found in the oil, and neither chlorinated dibenzodioxines nor furanes were detected.

A different approach to introducing plastic feedstocks into naphtha crackers is to use pyrolysis as a preliminary step. This has been demonstrated by BP at the scale of 25 kt/year in Grangemouth, Scotland. The pyrolysis reactor was a fluidised bed reactor operated at 500 °C [27]. The end-product was a waxy hydrocarbon mixture that could be mixed with naphtha (up to 20%) for feeding to conventional steam

crackers. Size reduction and removal of most non-plastics were required as pre-treatment steps [53].

PW streams with higher chlorine contents can result in corrosion and toxic emissions. This issue can be addressed in the initial steps of the process, for instance by excluding chlorine-rich wastes from the feedstock or by implementing a de-halogenation pre-treatment step, as was done in the BASF 15 kt/year plant, which was operated between 1994 and 1996 in Ludwigshafen, Germany [27,60]. Chlorine can be neutralised in the pyrolysis reactor using either lime sorbent, as is the case in the Hamburg fluidised bed pyrolysis process [45], or in a down-stream washing step, as is performed in the TEXACO process using ammonia as the sorbent [27]. Chlorine can also be the main product, as tested in the afore-mentioned AkzoNobel process with the Battelle technology. PVC-rich plastic solid waste was pyrolysed at 700–900 °C with steam to produce a fuel gas, while achieving high-level recovery of HCl [27,53]. The tests were carried out up to a scale of 300–400 kg/h feedstock input. Further reports on the commercialisation of this process could not be found in literature.

2.3. The cracking reactor

The afore-mentioned cracker process proposed in this work for plastics is based on the DFB concept. An outline of the cracker process for plastics is shown in Fig. 4. Into the cracker section, the plastics are fed together with dilution steam and part of the hydrocarbons that were re-circulated from the first cleaning (i.e., mainly oils $\geq C_5$) and fractionation (i.e., mainly unconverted ethane and propane) sections. Note that the first downstream cleaning steps after the cracker are highly dependent upon the feedstock type, whereas the fractionation and recovery sections are similar, regardless of the feedstock applied [20], and consequently, they can be integrated with the new plastic cracking facility. This means that the cracker unit for plastics replaces the existing naphtha/alkane cracker ovens, together with most of the first part of the gas separation (the yellow-shaded area in Fig. 4), in which the gas is filtered, cooled, cleaned of heavy hydrocarbons and impurities (organic and inorganic S-, N- and Cl-species), and dried. The majorities of the impurities are expected to be present in the product gas in inorganic form in the reductive environment, as previously stated, but also partially in organic form, which is easily condensable, and a solid residue [61–63]. Organically bounded Cl can be marked as especially environmentally problematic which needs to be handled together with other unwanted species in the overall process. However, researches have shown that the reducive environment during thermal processing of a feedstock rich in Cl resulted in low emission levels [64,65].

In the proposed cracking reactor, the heat for the cracking process is provided by the combustor section, which is shown schematically in Fig. 5. A combustion unit is required independent of the technology applied to provide heat to the cracking process and/or to incinerate the carbon streams that cannot be valorised and are condensed streams from the cracking process, where impurities, e.g. condensed organic fraction, following this stream can be handled in flue gas cleaning unit. In the proposed process, the combustor additionally serves as a re-generating unit for the bed material. The carbon-containing streams that are incinerated include the fixed carbon in the feedstock, carbon deposits on the bed material particles, the soot and the large PAHs that are separated in the gas filter, the PAHs that are separated during condensation, and other carbon-containing streams generated during the gas cleaning and separation steps.

To complete the energy balance of the process, the following strategies can be used: 1) combustion of part of the generated fuel gas (CH_4, H_2, CO); 2) introduction of direct electrical heating; and 3) feeding of PW of Groups 0 and *Biomass* to the combustor. The latter would also contribute to the intake of biogenic carbon to the system. Air or pure oxygen diluted with re-circulated flue gases (oxy-combustion) can be used for the combustion depending on the level of ambition for carbon recovery. With oxy-combustion, the goal is to achieve close to 100% carbon utilisation.

To obtain the required flexibility, the combustion reactor needs to be fully refracted to minimise heat losses. The only heat extracted from the reactor relates to the heat that is transported through the refractory to the water-filled panel walls, which serve as the mechanical structure of the combustion chamber (1 in Fig. 5). The steam for the process is produced through the cooling of the flue gases in the flue gas path (2 in Fig. 5) and through the extraction of heat during the looping circulation of the bed material between the cracker and the combustion, which is achieved by the introduction of an external particle cooler (3 in Fig. 5). The bed circulation in this type of reactor system is controlled by the gas flow through the combustion section. For this to be accomplished independently of the oxygenated flow (air or pure O_2), re-circulation of the flue gases is enabled.

The minimum level of carbon-containing species that needs to be oxidised in the combustion chamber is based on the requirements set for re-generation of the bed material and incineration of the non-valorised hydrocarbons. This also limits the extent to which electrification by direct heating of the cracker can be driven. The electricity is used

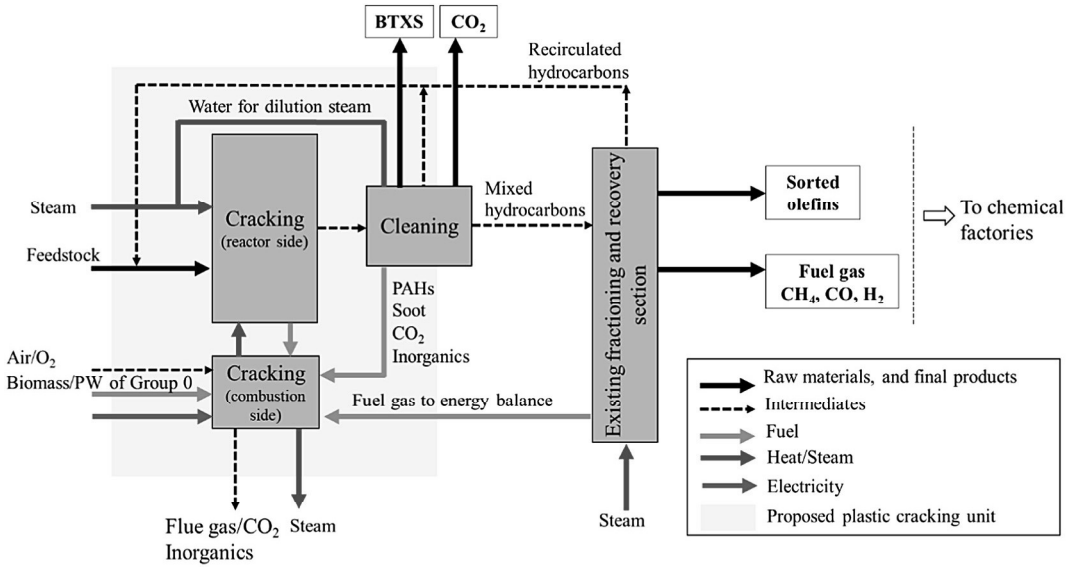

Fig. 4. Implementation of a cracker process for plastics within an existing naphtha/alkane cracking infrastructure.

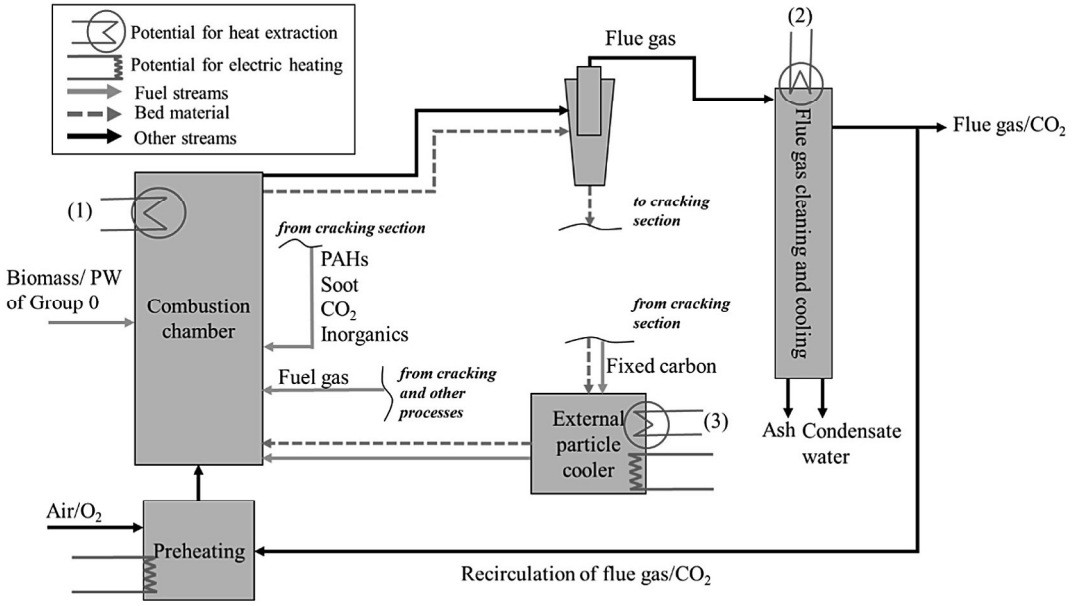

Fig. 5. Detail of the combustion section of the cracker. Indicated are the potential locations for heat extraction (1), (2), and (3), and for electric heating.

to pre-heat the air-flue gas mixture before it enters the combustion chamber, as well as for direct heating of the bed material within the circulation loop before it enters the combustor, as indicated by the blue coils in Fig. 5. The proposed placement of the electrical heaters is based on avoiding the development of a highly erosive environment in the combustion chamber, as well as to enable the flexibility to switch between heating using electricity and heating using fuel combustion.

Furthermore, to achieve close to 100% carbon utilisation, the air for combustion needs to be replaced with pure oxygen that is diluted with re-circulated flue gases. This will produce a nitrogen-free flue gas, which after cleaning and condensation results in a pure CO_2 stream that can be either utilised as carbon feedstock in down-stream synthetic processes or sent to storage in a geological site (CCS). The pure oxygen stream can be supplied through the electrolysis of water or by an air separation unit (ASU).

2.4. Petrochemical cluster in Stenungsund

The petrochemical cluster in Stenungsund is here used as a reference case to assess the feasibility of transforming the naphtha/alkane-based production of plastics into a thermal recycling process. In a petrochemical cluster, the initial step is to produce the chemical building blocks for the down-stream chemical factories. In the Stenungsund cluster, the bulk monomers are ethylene and propylene, together with smaller amounts of a wide variety of other hydrocarbons. These are produced in the of Borealis ethylene cracking plant by steam cracking of naphtha/alkanes, which is a side-stream from the refineries and up-grading of natural gas. The supply of ethylene to the chemical factories is complemented with imports of ethylene from other sites (20% of the total ethylene consumption of the cluster).

The bulk monomers are provided to four other chemical factories that produce polyethylene (Borealis), vinyl chloride (INOVYN), ethylene oxide (Nouryon, previously AkzoNobel), and aldehydes (Perstorp Oxo). An overview of the flows in the cluster is presented in Fig. 6, where the widths of the arrows are proportional to the corresponding mass flows. The cluster also includes a partial-oxidation unit for the production of syngas, a plant for the production of rapeseed methyl ester (RME), as well as other processes that use or provide raw materials to/from the afore-mentioned plants. There follows a brief description of the processes that are relevant to this work.

2.4.1. Ethylene cracking plant

The primary and secondary products of the cracking plant of Borealis in Stenungsund are ethylene and propylene, respectively. The inputs to the process are naphtha and alkanes (i.e., ethane, propane and butane). The plant consists of nine steam cracking furnaces, followed by an initial separation section for the removal of heavy oils and acid-gases and drying, which leads into a fractionation and recovery section, equipped with distillation columns, compressors and hydrogenation reactors. The feed is steam-cracked at 850 °C and the resulting stream is quenched to 200 °C before any separation takes place. The main streams that exit the separation processes comprise oils (≥C5), C4, propylene, ethylene, and lighter gases. The C4 fraction is used for the production of ethyl tert-butyl ether (ETBE) in a separate plant or sold to Perstorp Oxo, while the ≥C5 hydrocarbons are stored or sold, e.g., for energy purposes. In the cracking plant, the yields of ethylene and propylene are enhanced by hydrogenation of the alkynes and dienes present in the distillate. The remaining combustible light fraction (not shown in the figure) is mainly used internally for heat generation, although it is also exported as a fuel gas to the surrounding chemical factories [66].

2.4.2. Chemical factories

The PE-plant of Borealis produces PE species of different qualities. The main raw material is ethylene from the cracking plant, and there are also smaller amounts of other chemicals, such as co-monomers (e.g., butene, propane), organic peroxides, and H_2 [67].

The vinyl chloride plant (INOVYN) produces vinyl chloride monomer (VCM) and dichloroethane (EDC) from chlorine gas, ethylene, and oxygen. Chlorine is produced by electrolysis of an aqueous NaCl solution, in an adjacent chlorine plant. The EDC is an intermediate product in the production of VCM, although some excess production may also be sold as a final product [68].

Nouryon has different and inter-connected production plants in Stenungsund, including a plant that produces ethylene oxide (EO), which is used as the raw material for the subsequent production of glycol, ethylene amines, and surface chemicals. EO is produced by catalytic partial oxidation of ethylene with O_2 at high pressure and high temperature. In this process, CO_2 and water are produced as by-products in a parallel reaction. The CO_2 is recovered in a scrubber, and the clean CO_2 stream is sold as a product [69].

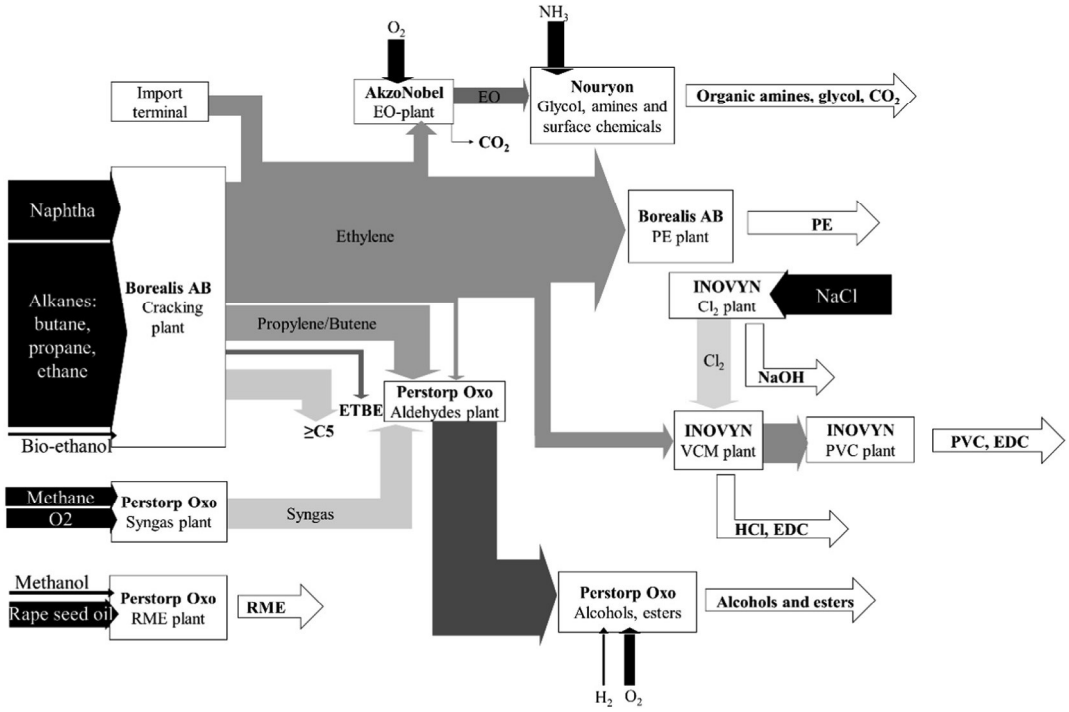

Fig. 6. Flows of chemicals in the Stenungsund chemical cluster. RME, Rapeseed methyl ester; ETBE, ethyl tert-butyl ether; EO, ethylene oxide; EDC, dichloroethane; VCM, vinyl chloride monomer; PVC, polyvinyl chloride; PE, polyethylene. The $\geq C_5$ species include fuel oil and pyrolysis oil. The widths of the arrows are proportional to the corresponding mass flows (except the white arrows, which represent final products). Based on the descriptions and flow values in the respective environmental reports [66,68–72].

Perstorp Oxo produces aldehydes from ethylene, propylene, and syngas. The aldehydes are subsequently used as feedstock to produce alcohols, carboxylic acids, and esters [70], as shown in Fig. 6. The syngas is generated on-site from natural gas via partial oxidation at 1400 °C and 40 bar, and it consists of roughly 50% CO and 50% H_2. Part of the H_2 is separated and used in other hydration processes [71]. In addition, Perstorp Oxo has an RME plant, which uses methanol and rapeseed oil as raw materials in a catalytic process [70].

3. Methodology

3.1. Experiments with plastic streams in the Chalmers DFB system

In this work, the Chalmers DFB system was operated as a cracking unit for plastic feedstocks. The aims of the tests were to assess the feasibility of scaling up a plastic cracking unit in a DFB configuration, and to obtain a first set of input data for estimating the heat and carbon balance of the proposed cracker. Furthermore, the results presented here provide information on the product distribution that can be typically expected from the cracking of plastics in this type of unit, and that can be compared to the data reported in literature for the pyrolysis/gasification of plastics in other types of units. Extensive experience with the cracking of plastic feedstocks in other types of rectors at different scales of operation can be found in the literature, as reviewed in Sections 2.1 and 2.2.

The Chalmers system consists of a 12-MW circulated fluidised bed (CFB) boiler and 2–4-MW bubbling fluidised bed (BFB) gasifier interconnected by two loop seals [73]. The gasifier (i.e., cracking reactor) and the seals are fluidised by steam. The bed material transports the heat between the combustion side and the cracking side, respectively, as described in Section 2.3. In the experimental campaign presented here, the bed material was active olivine, which had been activated by interaction with biomass ash in a previous run.

In this work, the DFB system was tested with feedstocks of Groups 1 and 2 to the cracking side, while wood chips (Group *Biomass*) was used in the combustion side, to provide the necessary heat for the process. The plastic materials chosen are two marginal examples of highly sorted and extremely mixed/unsorted plastic streams, respectively. They are: pure PE (Group 2); and a PW stream from the car-recycling process (Group 1), i.e., ASR. PE is also a model polyolefin plastic, in that it is representative of the most prominent plastic waste-stream in the world (recall the plastic waste-streams in Table 1). Moreover, PE is one of the most intensively investigated plastics in fluidized beds (see Table 5), which facilitates comparisons of the experimental results.

The operating conditions for the four steady-state operational cases investigated here are summarised in Table 6. The gasifier temperature was varied during the experiments, with the aims of studying its influence on the product distribution and of assessing the potential for a change in temperature to adjust the output of the cracking process. However, there was no intention to optimize the operation towards olefin production, and it is expected that under the conditions tested steam will be a reactant. This means that a fraction of the hydrocarbons derived from the plastics can be reformed or gasified, which results in a conservative estimate of the olefins produced directly from the PW in the cracker (Route A). A conservative estimate that is used in the subsequent evaluation of the performances of the cracker and the cluster.

The product gas composition was assessed by gas chromatography, and the content of aromatic hydrocarbons was analysed using the SPA method, as described previously [73,74]. The species assayed by gas chromatography were H_2, CO, CO_2, CH_4, and C_{2-3} hydrocarbons. The SPA method covers BTXS and other polyaromatics with boiling points up to that of coronene. To investigate the rate of fuel conversion, the total volume of dry gas per unit of feedstock was calculated based on a tracer gas (i.e., He), which was added to the gasifier [73]. With the measurements applied, the aliphatic hydrocarbons with four or more carbon atoms are not covered, so the gas composition is shown without this fraction in the *Results* section.

3.2. Proposed implementation steps

The petrochemical cluster in Stenungsund, as described in Section 2.4, is used as a reference to assess the feasibility of switching

Table 6
Summary of relevant operating parameters corresponding to steady-state operation with two plastic-containing streams in the 2–4-MW Chalmers DFB gasifier.

Feedstock to gasifier	Fuel flow, kg/h	Steam flow, kg/h	Steam-to carbon ratio, kg steam/kg $C_{feedstock}$	Bed temperature gasifier, °C	Raw gas temperature, °C	Mass flow of the bed material, tonnes/h
PE	118	215	2.0	780	710	n.a.
PE	114	215	2.1	655	620	n.a.
ASR	372	220	1.8	840	767	21
ASR	372	220	1.8	790	730	21

PE, polyethylene; ASR, automotive shredder residue; n.a., Not available.

the current feedstock to PW streams. The material flows shown in Fig. 6 are in Fig. 7 simplified to illustrate what is included in the heat and mass balance calculations. The box labelled *Cracking and cleaning* aggregates the cracking ovens and initial separation steps that are needed prior to fractionation, i.e., the separation of particles, heavy oils, water, and CO_2 from the cracker gases. The fractionation and recovery sections include the compression units, distillation columns, and hydrogenation reactors that are already present in the cluster. The box labelled *Chemical factories* accounts for all the demands for heat and hydrocarbons (feedstocks and fuels) of the chemical factories, excluding the RME plant, as it is totally independent of the cracking unit, as shown in Fig. 6.

We propose that the cluster be modified step-wise from its current state to near-100% carbon utilisation, facilitated by feedstock replacement and in combination with electrification and valorisation of the CO_2 streams into hydrocarbons. These modifications would be introduced in four subsequent steps (Implementation steps 1, 2, 3 and 4), which are summarised in Table 7, and the corresponding main flows are schematised in Fig. 8a–d.

An alternative implementation route: Implementation steps, 2b, 3b and 4b are as well define in the same table. The main difference between the two implementation routes is that the first route involves a transition to maximum electrification of the combustion side of the cracker, whereas in Implementation steps, 2b, 3b and 4b the combustor is fed with PW of Group 0 or feedstocks of the Group *Biomass*. In the case of using *Biomass*, the aim is to introduce biogenic carbon into the process, which will compensate for the carbon leakage from the life-cycle of the plastics and/or for the CO_2 emissions linked to the transportation of the recycled plastics. Feeding feedstock Group 0 or Group *Biomass* to the cracker side instead of to the combustor is also possible, although it is here regarded as a less interesting alternative due to the thermodynamic penalty related to: a low yield of olefins (Table 2); a high production of carbon (Reactions A1, A2 and A3), which would have to be combusted in any case; and/or a high yield of CO_2 (Reactions A2, A4), which would have to be separated from the product stream.

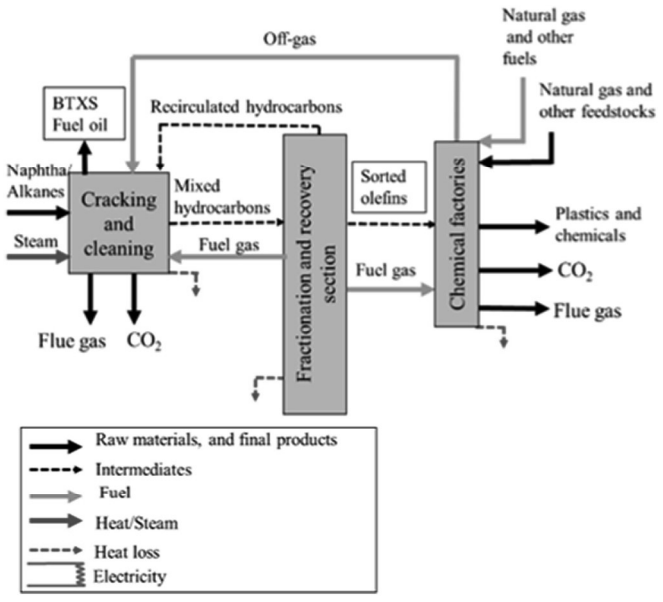

Fig. 7. Simplified schematic of the processes and flows in the existing Stenungsund cluster.

In Implementation step 1, plastic crackers are incorporated into the cluster and operate in parallel with the existing naphtha/alkane crackers. The olefins will, therefore, be produced in part from the plastics crackers and in part from the existing naphtha/alkane crackers. For each unit of feedstock, the plastics cracker produces more fuel gas than a cracker that uses naphtha/ethane. The dimensions of the plastics crackers are chosen such that the surplus fuel gas can be used to satisfy the demands for external fossil fuels in the chemical factories, as well as to replace the natural gas that is currently used as a feedstock for syngas production in the existing partial oxidation unit of the cluster.

In terms of the product distribution linked to the plastics cracker, there will be olefins and BTXS, while the fraction $\geq C_5$ will not exist because it will be re-circulated back into the cracker for further conversion. The BTXS can be, for example, exported for plastics production, thereby using these elements as building blocks elsewhere. For the cluster, this implementation step will entail a gradual fuel switch in the cracking plant, by bringing additional cracker units into operation and not interfering with the production of the chemical factories.

Table 7
Implementation steps proposed to achieve 100% utilisation of carbon in a plastics cracking plant within the existing chemical cluster at Stenungsund.

Implementation step	Goal	Heat sources in the cracker
0. Reference	Existing chemical cluster in Stenungsund	Combustion of fuel gas from naphtha/alkane cracker mainly
1. No fuel addition	Introduction of a plastic cracker in parallel with the existing naphtha crackers	Combustion of fuel gas from plastic and naphtha/alkane cracker
2. Feedstock switch	Phasing out of the naphtha/alkane cracker. The cluster is supplied by the plastic cracker only	Combustion of fuel gas from plastic cracker (with option to use ASU and oxy-combustion)
2b. Feedstock switch (PW Group 0 or feedstock Group *Biomass*)		Combustion of Group *Biomass*/Group 0 and side-streams (with option to use ASU and oxy-combustion)
3. Electrification	Utilise all the fuel gas to produce hydrocarbons	Electric heating and combustion of side-streams (with option to use ASU and oxy-combustion)
3b. Electrification (PW Group 0 or feedstock Group *Biomass*)		Combustion of Group *Biomass*/Group 0 and side-streams (with option to use ASU and oxy-combustion)
4. 100% carbon utilisation	Maximise the carbon utilisation, introduction of an electrolyser for H_2 and O_2 generation	Electric heating and combustion of side-streams under oxy-combustion conditions
4b. 100% carbon utilisation (PW Group 0 or feedstock Group *Biomass*)		Combustion of Group *Biomass*/Group 0 and side-streams under oxy-combustion conditions

ASU, Air separation unit. PW Group 0: Plastic waste with an apparent hydrogen-to carbon ratio of nearly 0, e.g., PET, PMMA. Group Biomass: lignocellulosic materials and natural textiles.

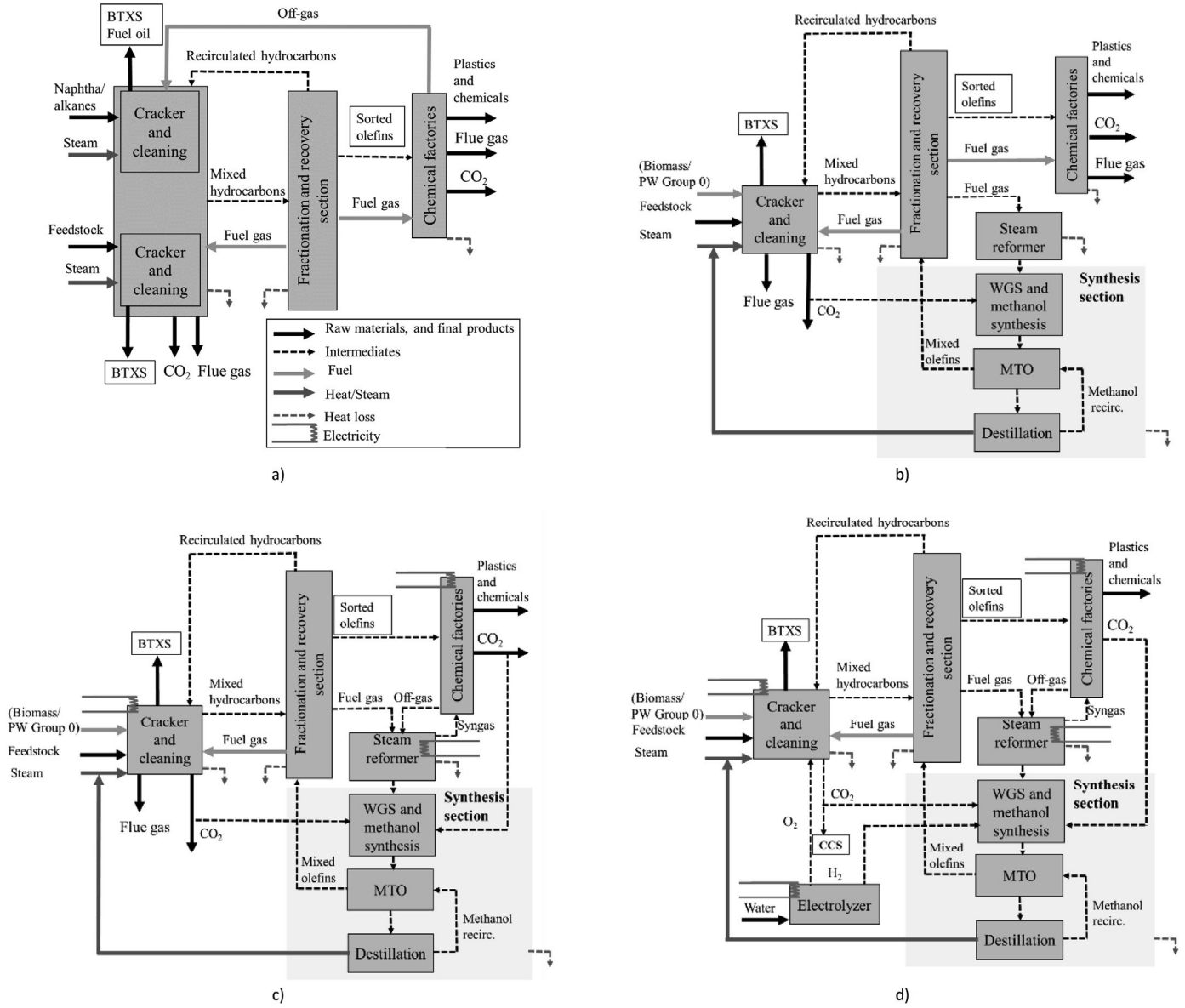

Fig. 8. Simplified schematics of the processes and flows in the proposed implementation steps (a–d), designed to achieve a complete switch from naphtha/alkanes to recycled plastic wastes and 100% carbon recovery. (a) Implementation step 1; (b) Implementation step 2/2b; (c) Implementation step 3/3b; (d) Implementation step 4/4b. MTO, Methanol to Olefins; BTXS, benzene, toluene, xylenes, styrene; WGS, water-gas shift reactor. The *Cracker and cleaning* term includes the initial separation steps in which the BTXS, water, and CO_2 are separated from the cracker gas. PW Group 0: plastic wastes with low hydrogen-to carbon ratio; Group *Biomass*: lignocellulosic materials and natural textiles.

In Implementation step 2, the production of olefins from the plastics cracking process is increased, so as to replace completely the naphtha/alkanes crackers. In this step, it is considered that the capacity of the cracker cannot be substantially larger than what will be needed in the subsequent steps. This is to avoid unnecessary over-capacity once the transformation of the cluster is completed. In practice, this means that in Implementation step 2 there will still be imports of olefins from elsewhere to the chemical factories.

As a result of the change of feedstock, the amount of fuel gas produced is more than is needed within the cluster. To utilise this fuel gas surplus, a synthesis process is introduced so that the fuel gas can be used as a raw syngas instead. Bearing in mind that the raw syngas that results from the cracking of the plastics consists mainly of CH_4 mixed with H_2 and CO, the simplest option is to produce CH_4 and export it from the cluster as synthetic natural gas (SNG). However, this will not promote advancement towards the eventual goal of achieving close to 100% recycling of the carbon in the plastics. For this reason, it is proposed instead to apply steam reforming of the raw syngas to generate pure CO and H_2 for the synthesis of olefins. The lay-out of the cracking plant in Implementation step 2 is shown in Fig. 8c.

The steam reforming process would ideally operate at low pressure, to enable full conversion at a relatively low temperature, thereby simplifying the subsequent electrification of the process. The reformed gas is thereafter pressurised to 120 bar and synthesised to methanol in a once-through methanol synthesis process, as proposed and demonstrated by Haldor-Topseo [75]. The produced raw methanol is then converted to ethylene in the Methanol-to-Olefins (MTO) process, as proposed by Honeywell UOP in their Hydro MTO process [76]. The olefins are separated from the unreacted methanol and water by condensation, and thereafter the olefins are sent to the fractionation section with the cracker products. The unreacted methanol is separated from water by distillation in a dedicated column and re-circulated back to the MTO reactor. The water and methanol remaining after recovery can be re-used as diluent steam in the cracker, thereby reducing the net consumption of fresh water in the process and enabling recovery of the remainder of the carbon in the water stream.

The MTO route is interesting for the cluster for several reasons. First, it increases the yield of olefins, which is the preferred feedstock for the chemical factories in the reference cluster. Second, the H:C ratio of the syngas obtained following blending a portion of the CO_2 separated during the cleaning of the cracker gas matches the requirement for methanol synthesis. Third, methanol can be exported and used as a base chemical in the external production sites of the industrial partners that constitute the cluster. Furthermore, including methanol as an intermediate in the cluster allows for the external import of renewable methanol from biomass, which in turn facilitates the introduction of biogenic carbon in the implementation steps that do not entail direct input of biomass.

In the alternative Implementation step (2b), the Group *Biomass* and/or the PW of Group 0 replace the fuel gas that is used in the combustor side of the crackers. Regardless of the fuel used in the combustor (fuel gas in Implementation step 2 or Group *Biomass*/PW of Group 0 in 2b), the combustor can operate in oxy-combustion mode to enable carbon capture and storage (CCS) and reduce the CO_2 emissions to the atmosphere. This requires the installation of an ASU unit to provide the necessary flow of oxygen.

Similar to Implementation step 1, step 2 or step 2b will interfere only minimally with the present production processes in the chemical factories, as the cracker continues to supply the chemical factories with olefins and with the fuel gas required for heating. This step can, therefore, be considered as a feedstock switch in the cracking process.

Implementation steps 3 and 3b have marginal effects on the feedstock switch, although they dramatically increase the utilisation of the fed carbon and eliminate the last fractions of the virgin fossil feedstock used in the cracker and the chemical factories. This is thanks to the extended use of electricity, which is introduced into three units: the crackers; the steam reformers; and the steam boilers.

Electricity replaces the full amounts of fuel gas (from the crackers) and off-gas (from the chemical factories) that were combusted in the previous step for the production of heat. This makes the fuel gas and off-gas available for the production of syngas via steam reforming, as shown in Fig. 8d. The syngas is utilised to increase the yield of olefins through synthesis, as well as to replace the syngas produced by the existing partial oxidation unit (Perstorp Oxo). All the CO_2 separated from the cracker gas in the cleaning steps and the part of the CO_2 produced in the chemical factories are in this step mixed with the syngas from the steam reformer to create the appropriate balance between carbon, hydrogen, and oxygen for methanol synthesis.

For the crackers, electrification means that the combustor evolves from operating as a regular combustion unit to being operated with electric air pre-heating and with electrical heating in the external particle cooler, as shown in Fig. 5. In the steam reformer, the electric heating will probably be achieved by external heating of a circulating bed material flow, in similarity to what is proposed for the combustion section. The advantage of this approach is that it retains the option to switch between electricity and combustion. For the chemical factories, electrification means that they do not consume any fossil fuel (fuel gas and off-gases) for heating purposes, and that the off-gases need to be free of nitrogen and contaminants prior to feeding them to the steam reformer.

In the alternative Implementation step 3b, combustion of feedstocks of Group *Biomass* and/or PW of Group 0 replaces the electric heating of the cracker. In both Implementation steps (3 and 3b), the CO_2 emissions from the combustor could be mitigated by using CCS, if an ASU and oxy-combustion are applied.

In Implementation step 4, the process enables close to 100% conversion of recovered plastics to chemicals. Most of the carbon that leaves the cluster as CO_2 is captured and converted to ethylene (and propylene) through synthesis processes, and in Implementation step 4b, a minor fraction is sent to storage (CCS). The sources of CO_2 in this implementation step are: the flue gas from the combustor of the cracker; the CO_2 separated from the cracker gas in the cleaning section; and the CO_2 produced in the chemical factories. In both Implementation steps (4 and 4b) oxy-combustion is introduced to generate a CO_2-rich stream from the combustion side of the cracker. To allow the use of this CO_2 within the synthesis process, a flue gas-conditioning step that consumes the excess of oxygen in the flue gas is required. This can be achieved by injecting additional syngas into the oxygen-containing CO_2 stream, heating up the mixture so the oxygen reacts with either the H_2 or the CO, and then cooling the stream. If the choice is geological storage of CO_2, the stream needs to be dried in addition.

In Implementation steps 4 and 4b, pure O_2 is produced by an electrolyser, where the amount of O_2 is calculated according to the demand of the combustor. The resulting flow of H_2 is mixed with the syngas before entering the synthesis process. The H:C ratio of the gas input to the synthesis is adjusted by adding CO_2 from the combustor, while the excess CO_2 is sent to geological storage.

Similar to the previous step, the off-gases from the chemical factories are sent to the steam reformer to produce syngas. Alternatively, the off-gases are burned in oxy-combustion mode, with oxygen provided from the electrolysers, followed by separation of the CO_2 and a cleaning step, before being sent to the synthesis process. However, depending on the level of effort needed (i.e., possible disruptions to production, increased carbon content of the off-gas streams), this carbon can be emitted to the atmosphere as CO_2 and compensated by renewable carbon atoms.

3.3. Assumptions made for the heat and mass balance calculations

The sizes of the hydrocarbon streams in the Stenungsund cluster are used here as input data to estimate the heat and carbon balances of the different implementation steps (Section 3.2). The cracker requires approximately 300 kt/year of naphtha and 1100 kt/year of alkanes for the production of ethylene, propylene, and fuel gas, which are subsequently supplied to the chemical factories [66]. In addition, 100 kt of natural gas are consumed in the cluster as feedstock for the production of syngas in the partial oxidation plant [77] and 12 kt are consumed as fuel in the chemical factories [68,72]. Approximately 180 kt of olefins are imported to the chemical factories from other olefin production plants outside the cluster [68,69,72]. Based on the data reported in the environmental reports for Year 2017 for the different production plants in the cluster, the energy demands of the chemical factories (fuels and electricity), as well as the demands for hydrocarbon feedstocks, which could potentially be provided by an alternative cracking process, are summarised in Table 8. As previously mentioned, the needs of the RME plant are not included because the plant is a stand-alone unit that is independent of the products generated in the cracker.

To estimate the carbon and heat balances of the existing cluster and the suggested implementation steps, the following assumptions are made for the different unit operations in the process.

For the cracker, the composition of the product stream is assumed to be similar to that obtained in the experimental part of this work with PE. The oil-rich fraction, i.e., that containing hydrocarbons $>C_5$, is separated in the first cleaning step (Fig. 4) and re-circulated back into the cracker, to increase the yields of olefins and lighter gases. In the cracker, this oil-rich stream will produce more olefins than the original plastics

Table 8
Summary of the demands for hydrocarbon feedstocks, fuels, and electricity in the chemical factories in Stenungsund. Data reported for 2017 (Borealis cracker excluded).

Feedstocks and fuels	Demand in Year 2017
Ethylene, C_2H_4	810 kt
Propylene, C_3H_6	180 kt
Syngas	150 kt
Fuel gas	900 GWh
NG fuel	344 GWh
Other fuels	9 GWh
Electricity	1200 GWh

feedstock. However, this conversion is not known within the proposed system, and it is arbitrarily assumed that 90% of the produced oil-rich stream is recycled into the cracker, and that it gives the same product distribution as the original plastic feedstock. Furthermore, the inorganic elements present in the plastics (either as part of the monomeric units of the polymer or as additives), such as Cl and N, are assumed to be converted into the stable products of HCl and NH_3, respectively, under cracking conditions [61,78].

To exemplify the alternative Implementation steps 2b, 3b, and 4b, the calculations are made specifically for 100% biomass being used to fuel the combustor, unless otherwise specified. This represents the extreme case in which the input of biogenic carbon to the cracker is maximised and stimulates a discussion as to the influence of introducing biogenic carbon into the cluster. Similar solutions with PW of Group 0 used as the fuel or blends of feedstocks of Group *Biomass* and PW of Group 0 as the fuel are also possible. However, the intake of biogenic carbon would be below that obtained with the extreme case of 100% biomass being fed to the combustion side of the cracker.

For the first gas separation down-stream of the cracker, it is assumed that water, PAHs, CO_2 and inorganics are completely separated from the remainder of the hydrocarbons (CO and H_2) generated during cracking. The heat demand in this step is estimated from the reference case with naphtha/alkanes as: the difference in the chemically bound energy of the hydrocarbons fed to and leaving the cracker unit minus the latent heat of the produced cracker gas exiting the cracker at 825 °C. This assumes that more or less all of the latent heat from the flue gas and none of the latent heat of the cracker gas are recovered.

For the steam reformer, the composition of the product gas is assumed to be at equilibrium at approximately 830 °C and 1 bar, and it is assumed that the unconverted CH_4 is re-circulated back into the reformer after passing through the MTO process. In the heat balance calculations, the heat demands of the reformer and cracker are aggregated and accounted for in the combustion section of the cracker. The estimated heat losses in the steam reformer (reaction side) refer exclusively to those related to the heat of the reforming reactions. In the cases that include an electrically heated steam reformer (Implementation steps 3 and 4), the heat losses also include those losses associated with the electrical heating.

The syngas required by the chemical factories is assumed to have a composition corresponding to that of a gas at equilibrium at 1400 °C and 40 bar, i.e., the operating temperature and pressure of the partial oxidation unit that currently produces syngas for the cluster [71]. This gives a gas with a H_2:CO ratio of 1.4, which the factories can use to replace the current natural gas consumption for the generation of syngas and H_2.

The synthesis section is assumed to consist of a methanol reactor operated at 120 bar, an olefins synthesis (MTO) reactor operated at 1 bar, and a distillation column for the unconverted methanol (water-mixed). This non-converted methanol fraction will vary in size depending on the preferred ratio of ethylene to higher olefins leaving the synthesis section. The heat required for distillation of the methanol-water mixture leaving the MTO process is assumed to be supplied by heat integration. In addition, an alternative case without heat integration in the synthesis section is considered, to estimate the impact of heat integration on the energy balance of both the cracker and the cluster.

The electrolyser, which feeds H_2 to the synthesis section and O_2 to the oxy-combustion process, is assumed to be a state-of-the-art atmospheric alkaline hydrogen plant, with an energy consumption of 4 kWh/Nm^3 H_2 at 1 bar [79]. This translates to a 75% energy efficiency based on the lower heating value (LHV).

In the cases with direct electric heating and electric boiler, the electricity demand is estimated as the equivalent to the energy input required (based on the LHV) when heat was supplied by the combustion of fuels.

3.4. Performances of the cracker and the cluster

Once the carbon and energy balances of the cracker and the cluster are established, efficiencies and other performance indicators are calculated, to compare the performance levels of the cluster and the cracker in the different implementation steps. Three efficiencies are defined.

Apparent efficiency of the conversion route. This indicator relates to the energy efficiency of generating the different products via a specific conversion route, i.e., Route A, B or C (Fig. 3). The product streams include olefins, BTXS, and syngas, which are the streams that are sold to the chemical factories. The apparent efficiency is calculated as the chemically bound energy in the product stream divided by the energy required for the production of such a stream via a specific conversion path. The allocation of the energy requirement to a reactant-product pair in a conversion path is based on the mass fraction of carbon of the corresponding reactant stream entering each unit.

Energy efficiency of the cracker and the cluster. The energy efficiency is estimated as the chemically bound energy in the product streams of the cracker and cluster, respectively, in relation to the total energy inputs to the cracker and to the cluster. The energy inputs account for the energy that is chemically bound in the fuels and feedstocks (based on the LHV of the dry part of the fuel), as well as the electricity input. The use of electricity for heating will, of course, not be an efficient use of the exergy, but the value of resources will be reflected by its system price in the energy system. This, however, is out of the scope of this work.

Carbon efficiency of the cracker and the cluster. The carbon efficiency is estimated as the total flow of carbon in the product streams in relation to the total inputs of carbon into the cracker and into the cluster, respectively.

In addition, performance indicators that relate to the overall goal of the transformation of the cluster are also evaluated. The driver for transformation of the cluster will depend on the context and regulatory framework of the business, the analysis of which is outside the scope of the present work. Nevertheless, to facilitate the discussion, several potential drivers are considered below.

Demands for CO_2 reduction by the Government. The CO_2 emissions that are accounted for are those leaving the plant through the stack as a result of the combustion of fuels for heating purposes, as well as those released through flaring of the gas. The pressure for emissions reductions can be directed towards: (1) reducing emissions from all sources; (2) reducing emissions from fossil sources, with the possibility to compensate for emissions from other sectors through the use of biomass or CCS technologies; and (3) achieving net-negative CO_2 emissions, whereby biogenic carbons can become more valuable as carbon sinks than as products.

For the reference case and for Implementation steps 1–4, the CO_2 emissions originate exclusively from fossil resources, which can only be mitigated by implementing oxy-combustion followed by geological storage. In Implementation steps 2b, 3b and 4b, there is the possibility of having CO_2 emissions from biomass combustion, depending on the fuel chosen (feedstocks of Group *Biomass* and/or PW of Group 0), and this can be considered as carbon-neutral. The CO_2 emissions are in these cases allocated to fossil and biogenic sources, respectively, based on the share of biogenic carbon entering each unit operation of the cracking plant. In the proposed system, this strict allocation is straight-forward, given that biomass, if chosen as the fuel, is only processed in the combustion side of the cracker, where it produces primarily CO_2.

Demand to increase the share of biogenic carbon in plastic products. This demand can be driven by the Government or by customers. This driver is only relevant to Implementation steps, 2b, 3b and 4b when using biomass as the fuel and relies heavily on the allocation method applied, which can be based on:

- Mass balance over the entire cracker, i.e., the fraction of biogenic carbon in the final product is the same as the fraction of biogenic carbon in the input to the cracking plant.
- Strict allocation in each process unit of the cracking plant, i.e., only the biogenic carbon that physically ends up in the final product is accounted for in this case.

With the strict allocation approach, only Implementation step 4b and cases in which biomass is fed to the cracker contribute to increasing the share of biogenic carbon in the plastic products, given that the CO_2 produced from the combustion of biomass becomes the carbon feedstock for the synthesis process.

Massive introduction of intermittent power sources, such as wind and solar, in the power sector would require corresponding balancing of power generation and/or consumption. The idea is that the cluster would be able to operate in the mode that is most economic, regardless of how many implementation steps are realised. This means that, in principle, operation according to implementation step 2 can be made even after the implementation of steps 3 and 4. The potential of the process to contribute to balancing the power network is discussed in terms of the available power when switching between operational modes. This option is relevant to Implementation steps 3, 3b, 4, and 4b, in which large electricity-consuming units are integrated into the process, i.e., electric boilers and electrolyser, and they can balance the power networks (recall Table 7).

Increasing the carbon recovery from PW, i.e., increasing the recycling quota. The carbon recovery from PW is here defined as the percentage of the carbon in the plastics feedstock provided to the cracker (cracking and combustion sides) that ends up in the final products. The carbon recovery rate has a direct impact on savings related to use of virgin fossil resources in the production of plastic goods.

Business as usual, whereby customers of the bulk products of the cluster are not willing to pay extra for recycled products. In this case, the main driver is the economic savings derived from the switch of feedstock in relation to the investment required in each implementation step. The basis for the economic calculations is described in the sections below.

3.5. Price of feedstock

The operational costs are estimated based on the prices for feedstock listed in Table 9. The average, high, and low prices for the period between November 2017 and November 2018 have been collated to allow a best guess of the feedstock price, as well as to assess the uncertainty related to market price fluctuations.

For liquefied butane, propane and ethane, these prices are based on the official spot prices at Mont Belvieu, Texas, USA [80] in the period November 2017 to November 2018. These spot prices are in line with the prices of propane and butane delivered as large cargo to plants in north-west Europe and traded in November 2018 [81]. For the cost estimation, it is assumed that the price relationship between propane delivered as large cargo and naphtha (89%) remained constant during the considered time period, where the relationship is derived from the propane and naphtha traded in north-west Europe in November 2018 [81].

To estimate the cost of the ethane off-loaded at a coastal cracker plant in north-west Europe from the US, the cost of the logistics needs to be included, to permit a fair comparison with competing feedstocks. As liquefied ethane is not cost-competitive in the existing European LNG market, it is here assumed that the cost of logistics for the liquefied ethane are equal to, or higher than, the market price for natural gas in Europe (given in Rotterdam) and the market price for liquefied ethane in the US (Mont Belvieu). Considering the average monthly prices for the period of November 2017 to November 2018, this difference is 9.8 €/MWh or 147 $/tonne, which is the cost estimated for the logistics of ethane used in this work. This is somewhat higher than that assumed in previous studies [82], although it is within the expected uncertainty level of the prices of the landed feedstocks at the cracker plant, which are purchased only partially on the spot market.

The price of ethylene is taken from contracts for ethylene that was delivered for free to plants in north-west Europe during 2018 [83].

The price of natural gas in Europe is taken from the market price at Rotterdam, TTF [84], where the cost of pipeline transport of the gas to the chemical cluster is calculated from the permit of the Swedish natural gas pipeline owner, which has regulated the 3-year cost coverage (2.014 billion SEK) based on a specific delivered volume (800 million Nm^3). This gives a cost for pipeline transport of 5.6 €/MWh [85].

The price of electricity is taken as the average price for the period from November 2017 to November 2018 on the Nord Pool power market for the region comprising Stenungsund (where the reference cracker plant used in this work is located) [86,87]. The average transmission cost is calculated by assuming constant power consumption year-round and applying the prices set by the network operator in the region (Vattenfall AB) [88]. The Nordic location implies that there are

Table 9
Assumed prices of the feedstocks. High and low periods indicate the lowest and highest prices registered for each feedstock since the end of 2017 due to market fluctuations. Average prices are shown in the units given by the source 2017.

	Average Price	Unit	Average Price	Low period	High period	Cost of logistics
			€/MWh	€/MWh	€/MWh	€/MWh
Oil brent	76	$/barrel	39.9	34.3	46.4	
Naphtha	501	$/t	35.1	26.5	38.9	
Propane	446	$/t	29.6	22.4	32.8	
Butane	446	$/t	30.0	22.6	34.7	
Ethane	188	$/t	12.2	9.8	19.0	9.8
Ethylene	1090	$/t	71.1	66.2	74.6	
Natural gas	22.3	€/MWh	22.3	18.6	28.7	5.6
Electricity	39.8	€/MWh	39.8	29.8	50.5	5.3
Mixed plastics, long-term	1000	SEK/t	8.5			
Mixed plastics, middle-term	0	SEK/t	0			
Mixed plastics, present	−900	SEK/t	−7.7			
Recovered wood as received	71	SEK/MWh	7.0	6.8	7.2	
Recovered wood, dry	69	SEK/MWh	6.7	6.5	6.9	
Contaminated recovered wood	0	SEK/MWh	0			
Forest residue as rec.	185	SEK/MWh	18.1	17.4	18.6	
Forest residue, dry[a]	169	SEK/MWh	16.6	15.9	17.0	
Wood pellets as received	267	SEK/MWh	26.2	25.8	27.5	
Wood pellets, dry ash-free[a]	263	SEK/MWh	25.8	25.4	27.0	

Currency conversion rates: USD/€ = 1.17, SEK/€ = 10.2.
[a] Recalculated prices on energy basis assuming 40% moisture for forest residues and 7% moisture for wood pellets.

modest CO_2 emissions associated with the production of the electricity used in the cluster.

Regarding the price of the recovered plastics, a relevant market reference is lacking, and since China blocked the import of mixed plastics waste during the Summer of 2018, the market has collapsed. In fact, the 7300 kt/year (Year 2015) of mixed PW that high-income countries used to send to China (recall Table 1) can now be assumed to be available in Europe at no cost. Therefore, the price of mixed PW in the mid-term perspective is set to zero in the economic calculations, under the assumption that the 16,000 kt/year of mixed PW, which currently are traded at a negative price on the global market [9], are available for chemical recycling. In the long term, however, and regarding large-scale chemical recycling, it is reasonable to assume that this PW fraction will acquire a market price. The estimate of the long-term price of this PW is here based on the current price of getting rid of mixed PW streams, which gives an indication of the economic driver needed for the collection and logistics aimed at making use of vast quantities of this waste fraction. This trade occurs on a contract-to-contract basis, and the price levels of most of these contracts during Year 2018 have been around −90 €/t, based on personal communications with persons active in the trading of recycled mixed plastic materials. Furthermore, it is assumed that the price of the mixed PW in the long term will be just above the market price for recovered wood, with a quality that does not require a boiler that meets all the demands for a waste incinerator (at present, this is around 7 €/MWh [89]; see below). Applying these assumptions, the long-term price of the recovered mixed plastics is estimated as 100 €/t.

The co-products produced in the cracker, benzene and >C5 hydrocarbons, are typically sold to produce petrol or fuel oil. Alternatively, they are sold to the chemical industry. Here, it is assumed that the price that the cracker receives for these products is equal to the price of Brent crude oil.

Applying the prices presented in Table 9, the resulting cost for producing olefins from the feedstock mix in the Stenungsund cluster is on average 578 $/t for the period of November 2017 to November 2018, encompassing a low cost level of 443 $/t and a high cost level of 683 $/t. This is in line with the estimated cost for olefins produced in the region during the first half of Year 2018 from propane and butane (around 500 $/t) or from naphtha (around 900 $/t) [90].

The cluster at Stenungsund has good opportunities to import various forms of biomass and PW to the cluster, owing to its strategic location close to a harbour and its good access to the railway system. Two examples of large, biomass-fired power plants can be used as a reference for logistic solutions that involve large volumes of biomass and PW, i.e., the DRAX power station in the UK [91], and Värtaverket in Stockholm [92]. The DRAX plant handles 12,000 kt/year of biomass, which are shipped to the plant from the US, providing an example of global logistics. In Sweden, where national biomass resources are available, Värtaverket exemplifies the combined local and global sourcing of biomass, where biomass from the Baltic Sea area arrives to the plant in ships and the domestic biomass arrives by train. In total, Värtaverket handles approximately 600 kt/year of biomass in central Stockholm.

In line with the ambition of creating a recycling plant, the plant should preferably be fed with waste wood that has a low content of inert materials, including metals and the remains of paints or coatings. The price of this waste fraction, here labelled as recovered wood, is given in the statistics for the Swedish market [89]. The flue gas cleaning (which needs to be installed in any case) allows also the use of waste wood fractions that include paint, which have a significantly lower price than the paint-free waste wood fractions and, in some cases, even have a negative price. This waste fraction is labelled as contaminated recovered wood and its price is assumed to be zero, as listed in Table 9. In the cluster, heat integration possibilities exist and have been studied [93]. However, that study has shown that it is difficult to accomplish an additional integration in a producing cluster as it requires extensive intervention with the existing process, which would interrupt production at the plant for too long a time period. In the same study, latent heat obtained from, for example, the quenching of the product gas is given, and it will most likely be sufficient for the drying of the biomass.

Based on the prices listed in Table 9, different cases are evaluated to obtain estimates of the total price of the feedstock under likely and extreme market conditions, in combination with different prices for PW (present−/middle−/long-term prices), as well as different choices of fuel provided to the combustor in Implementation steps, 2b, 3b and 4b (recovered wood/contaminated recovered wood). These cases are listed in Table 10.

3.6. Investment costs

A rough estimate of the level of investment required for the implementation of new equipment is presented here. The cost estimate is performed under the following assumptions related to the costs for the different process units.

For the cracker units using plastics as feedstock, the technology is based on a circulating fluidised bed (CFB) boiler that is connected to a bubbling bed, as previously described [24]. The capacities of these boilers are usually limited by the volume flow of flue gases in the convection path. To obtain an indication of the cost for a cracker unit based on this technology, it is assumed that the cost is similar to that of two plants that are dedicated to heat and power production and burning biomass with 50% moisture content. Here, the size of the cracker reactor is assumed to correspond to that of a bubbling fluidised bed (BFB) biomass boiler with a flue gas flow that is equal to the product gas flow from a cracker unit that uses 100% recycled plastics as feedstock. The combustion side of the cracker corresponds to a CFB boiler with a flue gas flow that is equal to that of a boiler that is burning biomass with 50% moisture content. The added costs related to the complexity and the increased need for refractory material of the dual bed system and gas treatment systems are assumed to be equal to the cost of the steam turbine and electrical generator that come with a combined heat and power plant, and, therefore, are not added to the cost of the cracker unit. This assumption is based on the cost evaluation of the DFB gasification system in the GoBiGas project and is similar to that of the cracker unit proposed here [94]. In the GoBiGas process, the gas cleaning was designed to remove contaminants from biomass, bark, and recovered wood ashes to the level at which it complied with the demand of the downstream methane synthesis process [24], and it is here judged to be sufficient also for the chemical cluster. The cost for heat and power plants based on fluidised bed boilers is derived from the actual investment cost for such plants in the region over the past 10 years, i.e., 13 MSEK/MW (1.275 M€/MW) [95]. To ensure sufficient redundancy within the system, it is assumed that seven parallel crackers are installed and that they can handle the volumes that correspond to the maximal volumes of the feedstocks for the investigated cases.

The costs for the steam reformer ($C_{inv,\,SR}$), methanol ($C_{inv,\,MOH}$),and MTO ($C_{inv,\,MTO}$) plants are assumed to follow the cost evolution associated with the scaling up observed for the 20-MW biomethane GoBiGas plant [95], where each of the three units is assumed to account for 50% of the scaled total cost. The investment cost ($C_{inv,\,i}$) for each one of these units (i) is described by:

$$C_{inv,i} = 11.7 \cdot \left(\frac{P_i}{20}\right)^{0.68} + 46.8 \cdot \left(\frac{P_i}{20}\right)^{0.44} \quad (1)$$

where the term '11.7' corresponds to the cost for the reactor systems, '46.8' is related to the auxiliary equipment and project costs, P_i corresponds to the scale of the considered unit (i) in MW of output, '20' corresponds to the reference scale, and '0.68' and '0.44' are the estimated scaling factors.

The reasoning behind this assumption is based on the accessibility of real cost data, in that: the costs for the GoBiGas plant are publicly

Table 10
Cases evaluated to estimate the total price of feedstock.

Total price of feedstock	Prices applied	Fuel to cracker	Fuel to combustor in Implementation steps 2b, 3b and 4b
Best guess, high	Average values	PW (long-term price)	Recovered wood
Best guess, low	Average values	PW (middle-term price)	Contaminated recovered wood
Expected maximum	High Period	PW (long-term price)	Recovered wood
Expected minimum	Low Period	PW (present price)	Contaminated recovered wood

PW, plastic waste.

available; the plant was built in the same geographical region using the same firms that would most likely be involved in any implementation of the proposed processes; and both the complexity of the process and the types of equipment resemble those of the proposed processes. To calibrate the cost level, the cost of the steam reforming is compared to the scaled cost of a newly installed steam reformer for natural gas at one of the refineries in the region [96] and the estimated cost for a methanol plant of a similar size listed in the literature [97]. The MTO process is a DFB process with down-stream gas separation. For the proposed implementation of the process, the fractionation and recovery sections already exist in the cluster, which significantly reduces the investment cost of the MTO process to that of a DFB complemented with primary distillation of non-converted methanol.

The cost for the electrolyser is assumed to be 0.75 M€/MW_H_2, which is within the range of prices for alkaline electrolysers reported previously [98]. Direct electrical heating of the crackers is accounted for during the initial installation, so the cost is limited to the heating elements. Here, the cost of the heating elements and their installation, as well as that of the electric boilers are estimated to be 0.1 M€/MW and 0.2 M€/MW, respectively. These values are based on experience from purchasing equipment for the GoBiGas project and the Chalmers power plant, and they are not further refined due to their weak impact on the total investment cost, as shown in the *Results* section.

In a case in which installing electrical boilers cannot be motivated due to interference with the production activity, the alternative is to increase the number of installed electrolysers and replace the fuel gas with hydrogen. In that case, there will be an excess of pure oxygen in the overall process. When biomass is used this could be balanced by increased storage of CO_2 at the expense of biogenic carbon conversion to olefins. Thus, the investment cost will be equal to the cost of the electrolysers, and the electrical demand for replacing the fuel gas will increase by 40%.

In Implementation steps 2, 2b, 3 and 3b, oxy-combustion is regarded as an option, which is discussed but not included in the calculated implementation steps. In this discussion, the costs associated with the ASU are estimated using Eq. (2) [97], where $\dot{m}_{O_2}$ refers to the size of the unit in tonnes O_2/day.

$$C_{inv,ASU} = 47 \cdot \left(\frac{\dot{m}_{O_2}}{1001}\right)^{0.85} \cdot 1.3 \quad (2)$$

The transition from air combustion to oxy-combustion should be planned for already during the installation of the cracker system, thereby controlling the cost for the implementation. However, there will be a need to extend the circulation and heat transfer systems to condition the CO_2, as well as to improve the cleaning process, so that the gas meets the specification of the synthesis process. It is arbitrarily assumed that the cost for implementing the carbon recovery system associated with oxy-combustion in the crackers are limited to 50 M€.

Recovered wood or biomass should preferably be dried before being used, so as to maximise the valorisation of the chemically bound energy and to take advantage of the excess heat of the cluster. This entails the installation of biomass dryers and connected fuel handling; the costs for such installations are taken from a previous analysis of the GoBiGas plant [95] and calculated according to Eq. (3).

$$C_{inv.drier} = 11.2 \cdot \left(\frac{P}{20}\right)^{0.67} \quad (3)$$

A logistic infrastructure similar to that applied today in fossil petrochemical products is assumed, where the logistics are based on transport by ship, which also covers the needs for storage and primary feeding of the feedstock to the process. It must be considered that there is an optimisation issue related to the sizes of the ships used and the number of possible loading locations. However, such optimization is outside the scope of this work, and a rough assumption of the logistic solution for a generic plant is here adjudged to be sufficient to give a first cost estimate for the feedstock logistics. For the bulk ships used for transportation, the storage, and the integrated part of the feeding system, a typical 50,000 DWT (dead-weight tonnage) bulk ship is assumed, i.e., 25 M€/ship [99]. The return trip of a vessel, including loading and unloading, is dimensioned for 30 days, where two ships are unloading at the cluster simultaneously and one additional ship is on stand-by to ensure redundancy in the feedstock supply. The cost of the feedstock terminal, which is also part of the primary system for feedstock feeding to the crackers, is arbitrarily estimated at 100 M€.

4. Results and discussion

In this section, the results are described and discussed with respect to technical feasibility, performance in relation to goals, other implementation aspects, and economic feasibility. First, the results from the experiments conducted at the Chalmers DFB gasifier are presented and extrapolated to the petrochemical cluster at Stenungsund for a case that involves switching of the feedstock to recycled plastics with 100% carbon utilisation. Second, the performances of the implementation steps, as detailed in Table 7 and Fig. 8, are discussed in relation to the objectives related to the transformation of the cluster. Third, the logistics and redundancy of the step-wise transformation are discussed. Fourth, the estimated costs of the feedstocks and required investments for the different implementation steps are presented.

4.1. Technical feasibility

The gas compositions obtained from the gasification of PE and ASR in the Chalmers DFB gasifier are summarised in Table 11. As previously mentioned, due to the limitations of the measurement systems applied, the compositions presented in the table are free of aliphatic hydrocarbons that have four or more carbon atoms. The yields of the measured cracking products in $kg/kg_{daf\ feed}$ are listed in the table for each experimental case, which corresponds to a closure of the carbon balances of 69% and 63% for the tests with ASR, and 77% and 54% in the cases of PE, for the high and low temperatures, respectively.

The carbon-containing species that are not measured by the applied instruments (μm-GC and SPA) can be related to soot, unconverted fixed carbon or to the unmeasured hydrocarbon fraction, i.e., aliphatic species ≥ C_4. In the case of PE, the most likely product (not covered by the measurements) is aliphatic hydrocarbons that would be recirculated to the cracker; while in the case of ASR some fixed carbon is also expected, which would go to the combustor for heat production [28]. The

Table 11
Experimental results of thermal cracking of polyethylene (PE) and Automotive Shredder Residue (ASR) in the Chalmers gasifier. Total others include: other aromatics than BTXS, CO, CO_2 and C_{2-3} alkanes/alkynes. Dry gas composition free of aliphatic hydrocarbons ≥ C_4, due to measurement limitations.

	PE (780 °C)	PE (655 °C)	ASR (840 °C)	ASR (790 °C)
γ (feedstock)	2	2	0.9	0.9
Yield of identified cracking products (kg/kg daf feed)	1.26	0.69	0.60	0.51
Product distribution (% wt. in the identified cracking products)[a]				
Methane	12	10	6	7
H_2	4	2	2	2
Olefins (ethylene, propylene)	28	48	8	11
BTXS	5	9	9	10
Total others[b]	52	31	75	71
Of which:				
Other aromatics	1	13	5	7
Other C_{2-3}	4	6	1	1
CO	10	6	9	9
CO_2	37	6	61	54

[a] Dry gas composition free of aliphatic hydrocarbons ≥ C_4, due to measurement limitations.
[b] Includes aromatics other than BTXS, CO, CO_2 and C_{2-3} alkanes/alkynes.

produced methane, CO, CO_2 and H_2 can be considered as a raw syngas that will be sent to steam reforming and synthesis.

The composition of the cracking products produced by steam cracking of PE and ASR in the Chalmers DFB system is comparable to the typical gas composition obtained from a naphtha/alkane cracker (see Table 2). At 655 °C, the concentration of olefins in the product gas derived from PE is similar to that derived from naphtha cracking; at a higher temperature (780 °C), the olefin yield decreases, mainly in favour of CO and CO_2.

The yield of carbon oxides is one of the most remarkable differences between the cracking gases produced in naphtha/alkane crackers and those produced in the present work, whereby the concentration of carbon oxides is 2–3 orders of magnitude higher in the present set-up than in the naphtha/alkane crackers. This may be the result of more intensive gasification and steam reforming of the hydrocarbons in the DFB system, which was not optimised for olefins production, due to, for example, the higher residence time of the gas and the presence of catalytic olivine. The high concentration of CO_2 underlines the need for a conversion route in which CO_2 is synthesised to olefins to achieve 100% carbon recovery, or with the use of CCS to avoid the corresponding CO_2 emissions.

The yield of olefins is clearly dependent upon the type of feedstock applied and the operating temperature. The PE and ASR cases at 780–790 °C highlight the influence of feedstock composition on the output of the cracking reactor, where the conversion of the feed into olefins (in kg/kg_{daf} feed) is 7-fold higher when cracking PE, and the level of methane is about 5-fold higher. This difference is in good agreement with the higher H:C ratio (γ-value) of PE compared to that of ASR. Similar yields of olefins were derived from PE at 655 °C and 780 °C, i.e., 33% and 35% of the carbon in the input feed (recalculated from the data in Table 11), respectively. However, at a higher temperature, the olefins are diluted by the higher yields of CO_2 and H_2 produced via gasification.

The yields of olefins are similar to those reported by Kaminsky et al. [33] for pyrolysis of PE at similar temperature. However, some differences can be found in the trends observed in this work compared to those in previous pyrolysis studies [29,33] of fluidised beds with PE. First, the production of aromatics is generally lower in the present work, and it decreases with increasing temperature, while the opposite trend has been observed by others [29,33]. Second, the production levels of CO and CO_2 were lower in the previous studies [29,33], as compared to the results presented here. These differences can be explained in part by the catalytic effect of the olivine applied in this work, in contrast to the use of inert silica sand by the Hamburg group. Compared to the work of Wilk et al. [25], who also applied an olivine bed for gasification of PE, the gas concentrations are rather similar, with a roughly 2-fold higher yield of CO_2 in the present case, and a 2-fold higher yield of CH_4 in the case of Wilk et al. [25].

Based on the experimental results presented above for PE, the energy and carbon balances of the cluster using plastics as feedstocks were estimated. It is assumed that the product distributions at the exits of the cracker are similar to those obtained with PE in the Chalmers gasifier. The complete set of results for the carbon and heat balances of all the implementation steps can be found in Appendices 1 and 2, respectively, in the form of Sankey diagrams. Here, the carbon balances of Implementation steps 4 and 4b are shown as examples, as these are the final steps in the transformation of the cluster when the aim is to achieve 100% carbon recovery. Implementation step 4b is calculated assuming biomass as the fuel fed to the combustor, which exemplifies the case with maximum input of biomass into the cracker, where the flow of biogenic carbon is highlighted in green.

As shown in the Sankey diagrams, in Implementation step 4, the final products of the cracking process are olefins, BTXS, and syngas, all of which are sold to the chemical factories. In Implementation step 4b, there is in addition the CO_2 stream, which is sent to geological storage. The conversion paths to generating these final products are: the direct formation of BTXS and mainly olefins (Route A); the formation of syngas for the chemical factories via steam reforming of the raw syngas from the cracker (Route B); the formation of olefins via steam reforming and the synthesis of raw syngas from the cracker or off-gases from the factories, respectively (Route B); and the formation of olefins from CO_2 (Route C), which can be generated through the combustion of heavier aromatics or biomass, or derived from the processes in the chemical factories (Fig. 10).

4.1.1. Apparent energy efficiencies of the conversion routes

The apparent energy efficiencies (recall the definitions in Section 3.4) of all the conversion routes in Implementation steps 4 and 4b lie in the range of 60%–82%. The values are summarised in Fig. 11. The lowest efficiencies are linked to the use of CO_2 from the combustion of biomass and other processes, respectively, for the synthesis of olefins. The losses in these conversion paths are those in the electrolyser, together with those experienced during gas compression, which supplies all the corresponding H_2 to produce a syngas with a H_2:CO_2 ratio of 3 for the methanol synthesis. Note that the apparent energy efficiency of the conversion path that involves the combustion of aromatics is nearly 10 percentage points higher than that of the other two routes via CO_2. This is explained by the reduced need for H_2 from the electrolyser when aromatics are formed in the cracker, as the formation of aromatics in the cracker yields H_2 as a by-product that can be used subsequently in the synthesis (Reaction A2 for feedstocks with γ-value of ~2; see Table 4). This high efficiency of olefin synthesis through the combustion of heavier aromatics confirms the advantage of taking this route instead of the alternative route via steam reforming when an excess of H_2 is generated in the cracking process.

As expected, the highest apparent energy efficiency corresponds to the direct production of olefins, since this entails only those losses related to the heating of the cracker, and the fractionation and recovery sections. With the introduction of biomass to heat the cracking unit in Implementation step 4b (instead of electric heating in Implementation step 4), the efficiencies of the conversion paths drop by 3–4 percentage points due to the higher losses linked to combustion, as compared to those related to the use of electricity. The conversion paths that do not require the cracker, such as those that proceed exclusively through the synthesis section, should have the same efficiencies in

Implementation steps 4 and 4b. This is evident in Fig. 11 for the formation of olefins from process-derived CO_2, where the difference between Implementation steps 4 and 4b remains at <1 percentage point. This can be attributed to the method of allocation rather than to an actual difference in energy efficiency between the conversion paths.

4.1.2. Energy and carbon efficiencies

The energy and carbon efficiencies that correspond to each Implementation step are summarised in Figs. 12 and 14, respectively, where panel (a) refers to the cracking plant and panel (b) refers to the whole cluster. Currently, the carbon efficiencies of the cracker and the cluster are approximately 85%, and the energy efficiencies are 80% for the cracker and 70% for the cluster. The introduction of modifications to the Reference case results in a gradual and relatively small drop in energy efficiency, i.e., 7 percentage points from the Reference case to the final Implementation step 4. The cases in which biomass is the fuel provided to the combustor (Implementation steps 2b–4b) have lower energy efficiencies than their counterparts with electric heating (Implementation steps 2–4). This is due to the largest heat losses occurring in the combustion side of the cracker (and electrolyser in Implementation step 4). The energy efficiencies of the modified cluster remain in the range of 60%–65%, which is similar to the estimated average energy efficiency of mechanical recycling (i.e., 65% [4]).

In Fig. 13, it is shown that the assumption made regarding heat integration of the synthesis section for Implementation steps 2–4 results in the energy efficiency being increased by a few percentage points compared to a similar case without heat integration. The increase in energy efficiency becomes more important as the synthesis section handles larger flows of gases, e.g., Implementation step 4b is the implementation step with a higher demand for synthesis. Nevertheless, the gain in efficiency remains at <5 percentage points for the cracker (Fig. 13a), corresponding to <4 percentage points for the entire cluster (Fig. 13b).

With regards to carbon efficiency (Fig. 14), the differences between the implementation steps are larger than those for energy efficiency, with 30 percentage points between the most (Implementation step 4) and least (Implementation step 2b) carbon-efficient implementation steps. Compared to the Reference case, Implementation steps 1 and 2 show decreases in carbon efficiency, due to the lower yield of olefins and the higher heat demand per unit feedstock when cracking plastic instead of naphtha/alkanes, which also implies higher losses of carbon in the form of CO_2 emissions to the atmosphere. Introducing biomass as the fuel in the cracker (Implementation step 2b) decreases the carbon efficiency even further, since biomass has a higher carbon-to-energy ratio than a fuel gas derived from the cracking of naphtha/alkanes and plastics.

With the use of electric heating in the cracker in Implementation step 3, the carbon efficiency increases to 95%, thanks to the additional production of olefins through synthesis of the excess fuel gas. Using biomass as the fuel instead of electricity (3b compared to 3) implies an additional loss of carbon in the form of CO_2 emissions with the flue gases, similar to when steps Implementation steps 2 and 2b are compared.

In the final Implementation steps (4 and 4b), the objective of close to 100% carbon efficiency is achieved. In Implementation step 4b, 92% of the inputted carbon ends up in products, as shown in Fig. 14, while 8% can be captured for storage. Close to 100% carbon efficiency can also be achieved in Implementation steps 2, 2b, 3 and 3b if an ASU and oxy-combustion are combined with geological storage (not shown in the figures).

4.2. Performance in relation to set goals

Demands on CO_2 reduction. If the aim of executing a transformation of the cluster is to reduce the net CO_2 emissions, the benefits are accrued only in Intermediate steps 3 and 4, as shown in Fig. 15, whereas the Implementation steps 1 and 2 yield emissions that are 40% and 70% higher, respectively, than those of the Reference case. The incurred penalty of the higher CO_2 emissions in the intermediate step 2 may be acceptable as a temporary transition stage leading up to Implementation steps 3 and 4, in which the CO_2 emissions are reduced by approximately 80% and 100%, respectively. Alternatively, the CO_2 emissions from the cluster could be reduced by 80% (compared to the Reference case) also in the intermediate step 2 at the expense of installing an ASU and oxy-combustion unit so as to have the option of geological storage.

If the CO_2 emissions that originate from biomass (Implementation Route 2b, 3b and 4b using biomass) are regarded as carbon-neutral, Implementation steps 2b and 3b perform better than the Reference case, with reductions in fossil-CO_2 emissions of 20% and 80%, respectively, which could become net-negative emissions of 300 kt/year and 800 kt/year, respectively, if oxy-combustion is implemented. Implementation step 4b, which already incorporates oxy-combustion, gives a net recovery of CO_2 from the atmosphere of 300 kt/year.

Demand to increase the share of biogenic carbon in the plastic products. Following an allocation rule based on the mass balance, Implementation steps 2b, 3b and 4b with biomass as the fuel confer the additional benefit of increasing the share of biogenic carbon in the final products from the cracker with each round of recycling. This is exemplified in Fig. 16, for Implementation step 4b, where the share of biomass in the input to the cracker is 25% (on a carbon basis) and the produced plastics are close to fossil-free after 10 cycles. This implies that the existing plastic stock will be 'greened' in approximately 5 years, assuming a life-time of 6 months for a generic plastic product and assuming that the same plastics are recycled over and over.

With a strict allocation rule, Implementation step 4b will still ensure that 25% of the carbon in the produced olefins originates from biomass. This is clear when following the flows of biogenic carbon in Fig. 9, where roughly 80% of the inputted biogenic carbon is incorporated into the product via synthesis. In contrast, for Implementation steps 2b and 3b, all the biogenic carbon is released to the atmosphere as CO_2 (see corresponding carbon balances in Appendix 1) or captured and stored if oxy-fuel is applied. Thus, a strict allocation rule leads to the conclusion that the addition of biomass does not contribute to the greening of the plastic stock. The alternative is to feed the biomass to the cracker, so as to be able to transfer the biogenic carbon atoms to the final product. However, this will be at the expense of the thermodynamic penalty associated with the use of a feedstock with a low apparent hydrogen-to carbon ratio, such as biomass, in the cracker.

Massive introduction of intermittent sources into the power system. The consumption of electricity by the cluster is in the range of the amounts of power generated by large power plants, and this will make the cluster an important and stabilising factor for the load curves of the electrical grid. As shown in Fig. 17, the electricity consumption is in the range of 180–250 MW in the Reference case and in Implementation steps 1 and 2, while this demand increases significantly with Implementation steps 3 and 4 owing to the introduction of the electric heating unit and the electrolyser, and it reaches a maximum of 1200 MW in Implementation step 4b.

In the switch of operation from Implementation step 3 to step 2, the electrical demand of the plant can be reduced from roughly 1000 MW to 200 MW (Fig. 17). Here, there will be a hierarchy of time response and durations connected to the characteristics of the various processes that are electrified on how the potential can be utilised to balance the electrical power grid. This option could be included in the power reserve and available occasionally during periods of severe power shortage. A drawback of this switch is the increased CO_2 emissions to the atmosphere (see Fig. 15 for CO_2 emissions), which will reduce the attractiveness of this switch for the power industry, as it could prevent them from meeting their emissions targets, provided that they will be accountable for the emissions. This drawback could be avoided by having an ASU and operating in oxy-combustion mode to allow for geological storage of

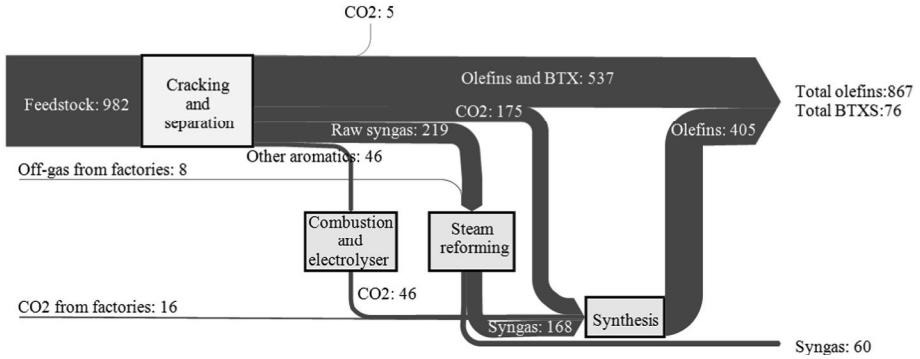

Fig. 9. Carbon balance in Implementation step 4 (ktC). The thicknesses of the arrows are proportional to the respective flows of carbon. The *Cracker and separation*' unit includes the cracking reactor, the first cleaning unit, and the fractionation and recovery sections.

CO_2. When an ASU is not an option, Implementation steps 2b, 3b and 4b using biomass as fuel to the combustor is more attractive, as a movement from Implementation step 3b to 2b will entail a smaller fraction of the CO_2 coming from the fossil part of the feedstock (see Fig. 15). The share of fossil-CO_2 in the total emissions would be reduced over time, as the recycled plastic will consist of more and more renewable carbons (see Fig. 16).

If operating according to Implementation step 4, which already incorporates oxy-combustion, a switch to operating according to Implementation step 3 would impose a serious challenge, as treatment of the entire flue gas from the combustor will be changed and upgrading of the CO_2 will be stopped. In this case, the ASU becomes crucial in enabling the switch of operating mode. By applying the ASU, the electrical demand (approximately 200 MWh/kt O_2 [100]) will be reduced by around 95%, as compared to when the O_2 is produced as a by-product from hydrogen production by splitting water (approximately 4000 MWh/kt O_2). While the ASU is operational, the combustion, gas cleaning, and CO_2 upgrading (including compression) can be operated continuously. The CO_2 produced from the combustion will, in this case, be sent for storage instead of being used as a feedstock for olefin production. This would be especially beneficial in Implementation steps 2b, 3b and 4b using biomass as fuel to the combustor, as it would increase the net extraction of CO_2 from the atmosphere.

An alternative to using an ASU in Implementation step 4b is to dimension the electrolysers so that 100% of the carbon is utilised to produce products during periods of high availability of electricity, i.e., the capacity of the electrolyser would have to be approximately 50% higher. In this case, approximately one-third of the oxygen produced will be in excess and can be stored for usage during periods of electricity deficit in the power network. In the latter situation, the load of the electrolysers will be reduced (or even eliminated) and the oxygen will be used for oxy-combustion, such that the CO_2 can be sent for geological storage. However, it is deemed that the additional cost for the electrolyser, as well as the sporadic liquefaction of the CO_2 and O_2, respectively, will raise more serious economic and technical challenges than the solution with ASU described above.

Carbon recovery from plastics. The rate of carbon recovery from the PW inputted to the cracking plant is summarised in Fig. 18. For Implementation steps 2b, 3b and 4b, the error bars indicate the possible range of carbon recovery rate, where the upper and lower edges correspond to using *Biomass* and PW of Group 0 in the combustor side, respectively. The benefits in terms of carbon recovery are clear from the first implementation step, in which about 70% of the carbon in the plastic feedstock is recovered in the form of new products. At this step, the rate of carbon recovery is similar to that obtained during mechanical recycling. Advancing to the subsequent implementation steps ensures

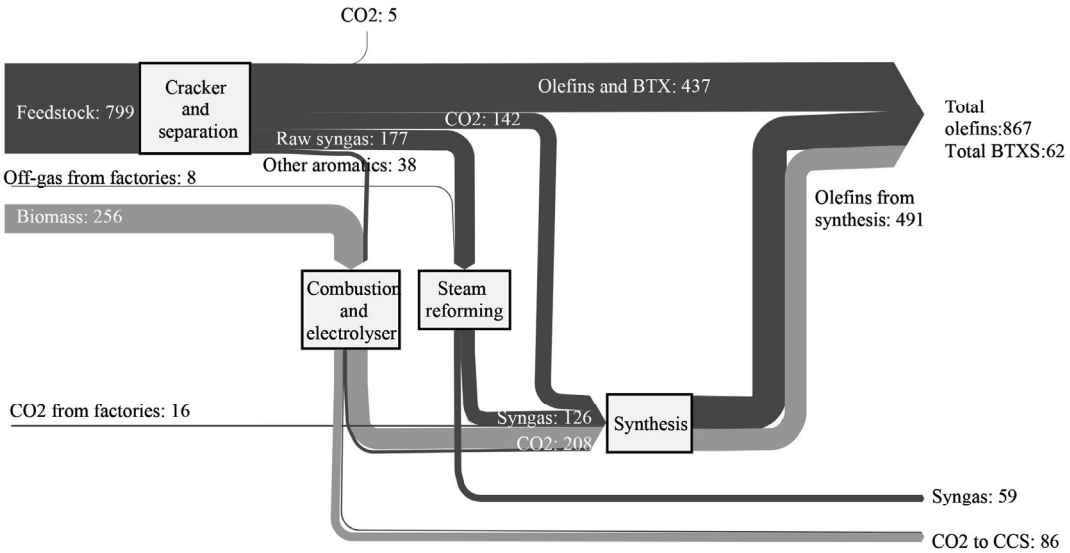

Fig. 10. Carbon balance in Implementation step 4b (ktC), assuming that a fuel of the Group *Biomass* is fed to the combustor. The thicknesses of the arrows are proportional to the respective flows of carbon. The Cracker and separation unit includes the cracking reactor, the first cleaning unit, and the fractionation and recovery sections. Green, Carbon originating from biomass; Blue, carbon originating from plastics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

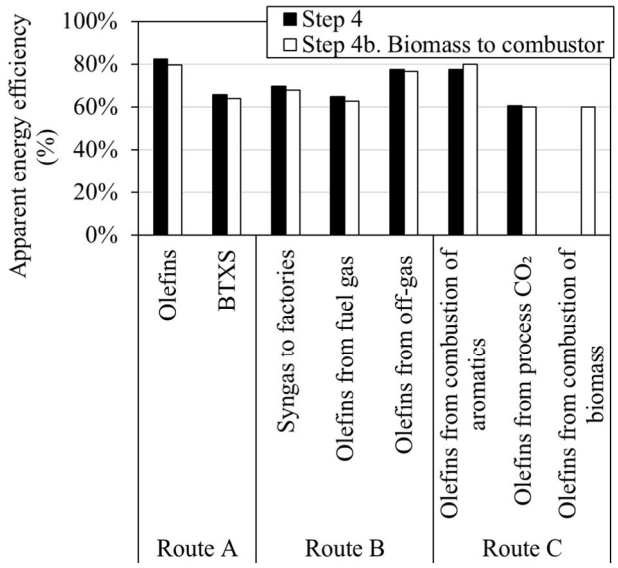

Fig. 11. Apparent energy efficiencies of the different conversion paths into final products (i.e., olefins, BTXS, and syngas). Route A involves direct production from cracking. Route B is via steam reforming (and synthesis). Route C is via CO_2 and synthesis with electrolysis. A fuel of the Group *Biomass* is assumed to be fed into the combustor in Implementation 4b.

that carbon recovery progresses to achieve close to 100% recovery from the PW stream in step 4.

The rates of intake and recovery of plastic wastes have the direct consequence of decreasing the dependency of the cluster on newly extracted fossil resources. The consumption of carbon resources (fuels and feedstocks) in the cluster is summarised in Fig. 19. Note that in Implementation step 2 (and 2b) there is a remaining fraction of fossil feedstock to the cluster, which corresponds to the annual import of olefins to the factories, i.e., 180 kt. As described in Section 3.2, this part of the feedstock was not replaced by PW in Implementation steps 2 and 2b, so as to avoid installing a substantially larger cracking capacity than would be needed in the subsequent steps.

Already at Implementation step 1, the recycling process increases the recycling quota by absorbing >700 kt/year of PW, despite the penalty incurred from increasing the CO_2 emissions by 370 kt/year (Fig. 15), as compared to the Reference case. This also means a net saving of virgin fossil feedstock of approximately 9 TWh annually. In Implementation step 2, the recycling quota is more than doubled compared to the previous implementation step, and the net saving of virgin fossil feedstock (relative to the Reference case) is equivalent to 20 TWh annually. Again, this is achieved at the expense of increasing CO_2 emissions, which are 660 ktCO_2/year higher than in the Reference case (Fig. 15).

4.3. Other implementation aspects

4.3.1. Logistics

Regarding the logistics of resources, a cluster of size similar to that in Stenungsund requires annually between 1000 kt and 1300 kt of recycled plastics as feedstock (recall Fig. 19), which corresponds to 3–4 kt/day, to phase out completely the use of primary fossil resources, such as naphtha/alkanes. The demand for plastics of the cluster is in the range of 6%–8% of the 16,000 kt/year PW that is exported from high-income countries to low-income countries. These quantities of PW require a global rather than a regional logistic network to secure the long-term feedstock supply, i.e., local on-shore handling must be minimised. Therefore, the assumed transport by ship is considered a suitable logistical solution. Under the assumptions stated in Section 3.6 for the logistics, eight ships would be needed to cover the needs of the proposed cluster.

Comparing a mix of compressed plastics with, for example, naphtha reveals that they have rather similar energy densities and chemical compositions. The main difference is that the mixed plastics are in the solid phase and the naphtha is in the liquid phase, which complicates the on- and off-loading of the feedstock. In addition, in a system such as the one proposed here, there will be logistics associated with the ash streams generated and with the bed material required in the fluidised bed reactors, which have not been covered in this work.

For Implementation steps 2b, 3b and 4b, and assuming that the fuel to the combustor is residual wood with 20% moisture content, the annual flows of biomass are in the range of 650–750 kt. This corresponds to a daily flow of approximately 2 kt of wood, which matches the need of a regular-sized pulp mill. This flow is roughly 1/16th of the need of the DRAX plant in UK and it is in the same range as that of Värtaverket in central Stockholm. This indicates that it is feasible to transport the required biomass flows to transform the cluster, probably by using a combination of locally and internationally sourced biomass. In addition, compared to the Värtaverket plant, the Stenungsund plant has the advantage of not being located in the centre of a crowded urban area.

4.3.2. Redundancy

A petrochemical cluster such as that discussed in the present work is typically shut down for major revisions only every 6 years. This means that the implementation needs to be feasible under continuous operation and to be restricted to what is allowed through reducing the redundancy of the process. Based on these criteria, we propose that the major part of the installation should be constructed on land that is available in the direct vicinity of the present cracker and fractionation units. Despite the short distance between the present and new locations, it will be necessary to deliver the gas from the new crackers for recycled plastics to

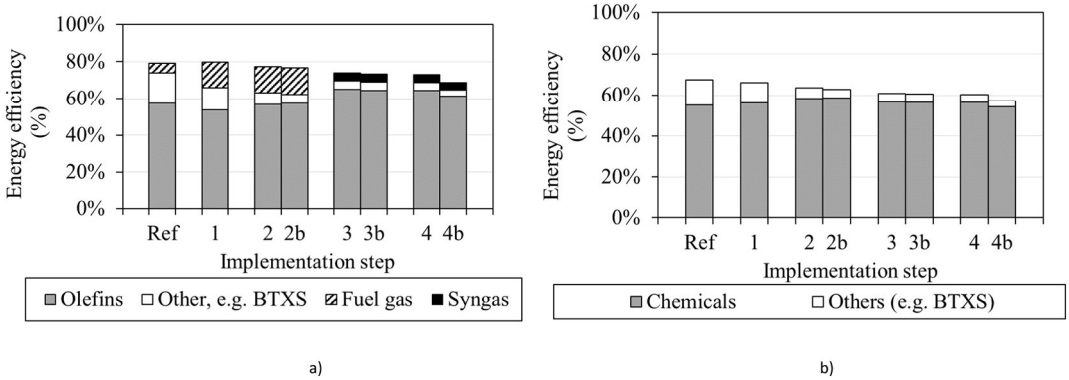

Fig. 12. Energy efficiencies in the Reference case and the four implementation steps proposed to achieve 100% carbon recovery. a) Cracking plant; b) Cluster. A fuel of the Group *Biomass* is assumed to be fed to the combustor in Implementation steps 2b, 3b and 4b.

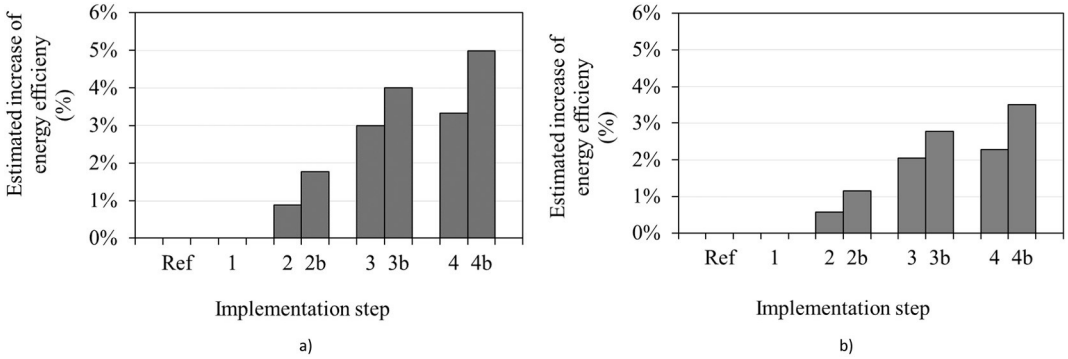

Fig. 13. Estimated marginal increase in efficiency (percentage points) when the synthesis section is heat-integrated. a) Cracker plant; b) Cluster. Fuel of the Group *Biomass* is assumed for the combustor in Implementation steps 2b, 3b and 4b.

the fractionation and recovery sections at ambient temperature. This is to avoid the use of complicated piping arrangements between the plants, and to ensure that the implementation can be executed during a short shut down of just one of the present fossil crackers at a time. The same strategy needs to be applied when progressing from Implementation step 2 to step 3 and, subsequently, to step 4. Here, the installation and subsequent operation of the steam reforming and downstream synthesis processes, respectively, need to be separated into two parallel production lines, so as to provide redundancy to the process, and more importantly, to ensure the continuous operation of the costly equipment introduced during Implementation step 2. Furthermore, Implementation step 4 will most likely not be possible to execute if the combustion side of the plastics crackers is not adequately prepared for oxy-combustion already from the beginning, as it will probably be too complicated to re-build the combustion side of the cracker from the originally intended air combustion unit to an oxy-combustion unit.

4.4. Economic feasibility

In Fig. 20, the estimated annual costs of the feedstock, fuels, and electricity for the various implementation steps are shown, based on the data presented in Table 9. The white bars in the figure indicate the range of best guesses for the total price of the feedstock, where the lower and upper edges are calculated according to the data in Table 10. The middle-term price for PW (0 €/tonne) applied in the estimation of the low best guess is judged to be reasonable during the period when the competition for PW is low. This price implies that a limited number of plants of this type and size are in operation, as each one of the plants could consume 6%–10% of the 16,000 kt/year of PW that are globally assumed to be available at zero price.

The effects of the highly volatile feedstock prices are indicated by the black bars in the figures, where the upper and lower edges correspond to the expected maximum and minimum total prices for the feedstock (recall Table 10). Note that the spot price during Year 2018 fluctuates in the range of ±20% relative to the average price, which can lead to extremely low prices under specific market conditions.

Focusing on the estimated average prices (white bars), replacement of the virgin fossil feedstock with PW and recovered biomass, i.e., going from the Reference case to Implementation steps 1 and 2 (or 2b), results in a significant cost reduction even in the long-term, which is clearly evident in Fig. 21. When Implementation steps 3 (or 3b) and 4 (or 4b) are performed, the reduction in the cost of the feedstock in relation to the Reference case is lower due to the reduced need for fuel when electric heating is introduced (recall Fig. 17). Implementation step 3b is an outlier in this respect, as the heat demand of the cracker is provided by the combustion of biomass rather than by electrical heating, and the reduction in the cost of the feedstock, especially imported ethylene, will compensate for the additional electricity use. The variation in price of electricity (±25% from the average) has a strong influence on the last two implementation steps, and as shown in Fig. 21 (black bars), during some time periods it overtakes the entire benefit of using recycled plastics and biomass.

Fig. 22 shows the incremental investment costs of the proposed implementation steps, together with the final cost after Implementation step 4. The complete list of unit operations and their sizes are summarised in Appendix 3. Depending on how many implementation steps are employed and on whether or not one wants to move to Implementation steps 2b, 3b and 4b, the costs for a plant operated with 100% recycled feedstock will be 1600 M€ to reach Implementation step 2 and 2000 M€ to reach Implementation step 2b. If there is a need to focus on reducing further the CO_2 emissions and on reaching close to 100% carbon recovery this will incur additional investments of 1300 M€ to

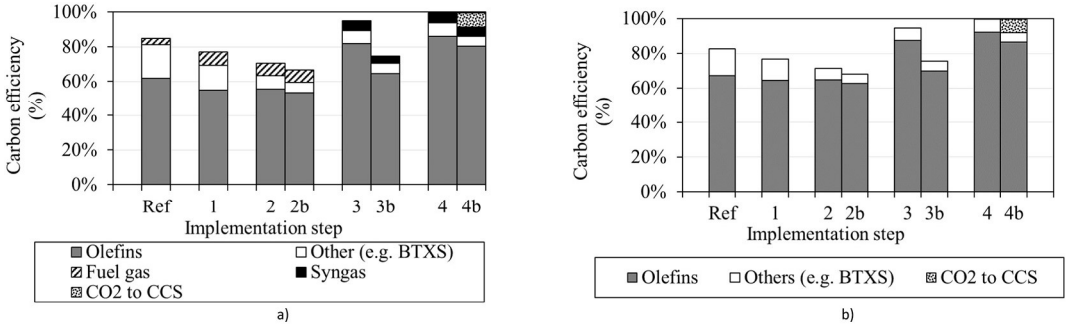

Fig. 14. Carbon efficiency levels in the Reference case and the four implementation steps proposed to achieve 100% carbon recovery. a) Cracker plant; b) Cluster. In Implementation steps 2b, 3b and 4b, the fuel in the combustor side is assumed to be of the Group *Biomass*.

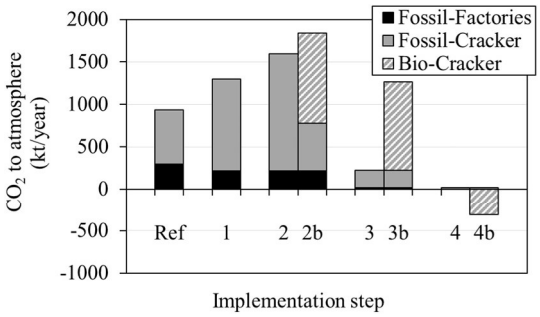

Fig. 15. Net fossil and biogenic CO_2 emissions from the cluster in the Reference (Ref) case and in Implementation steps 1, 2, 3 and 4, as well as in the alternative Implementation steps 2b, 3b and 4b using a fuel of the Group *Biomass* in the combustor.

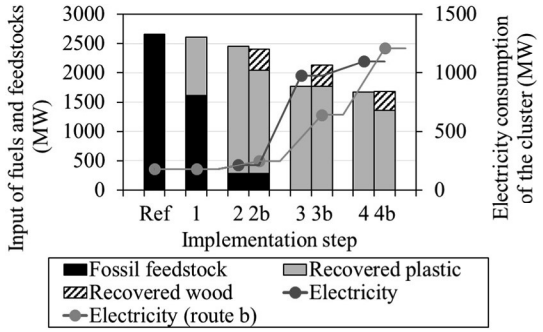

Fig. 17. Energy inputs to the cluster, fuels, feedstocks and electricity. Recovered wood as fuel to the combustor in Implementation steps 2b, 3b and 4b.

implement step 4 and 1500 M€ to implement step 4b. While it is more expensive, Implementation steps 2b, 3b and 4b creates additional flexibilities that can be exploited in the future, as discussed above.

To enable the possibility to switch between operating modes Implementation steps 4b and 3b, the additional cost of the ASU is in the order of 80 M€ (not included in the figure), or 2% of the total investment cost in Implementation step 4b. This unit will not be used most of the time, unless some other use is found for the generated O_2. In this context, there is scope for unconventional uses of this side-produced O_2, for instance, to oxygenate coastal areas and lakes that are subject to eutrophication [101] However, the infrastructure, requirements, flexibility, and costs associated with this application need to be evaluated.

The energy and mass balance calculations indicate that the size of one of the total of seven crackers that are proposed to be installed during Implementation steps 1 and 2 would correspond to a cracker with a feedstock input of around 400 MW. This size, scaled on the basis of gas flow, corresponds to a wet biomass BFB boiler with capacity of approximately 40 MW and a connected CFB combustion reactor of approximately 60 MW. To enable a step-wise implementation, without causing operational down-periods during the transitions between the steps, the steam reforming, methanol synthesis, and MTO processes are placed in two parallel production lines. Here, it is also necessary to decide whether or not to go for Implementation steps 2b, 3b and 4b, as the sizes of the process units will differ significantly depending on the selected route.

Considering the investment costs, Implementation steps 3 and 4 will represent roughly 75% of the cost of Implementation steps 1 and 2, while they does not induce any additional production cost reduction. This is shown in Fig. 23, where the annual cost reduction related to the feedstock (including electricity) is divided by the estimated accumulated investment costs for the different implementation steps, to give an indication of the payback time (excluding financial costs and other variable costs, e.g., costs for personnel, CO_2 tax, ash disposal, etc.).

Among the cases investigated, only Implementation steps 1, 2 and 2b are deemed to be associated with a reasonable risk for investment, with an indicative payback time of ≤5 years. Therefore, in a business-as-usual situation, only Implementation steps 1, 2 and 2b can be justified. It is noteworthy that even by adding the cost of emitting CO_2 at the present price (20 €/t_{CO2}) or at the highest price (123 €/t_{CO2}) considered in the scenarios explored by the International Energy Agency [21], the conclusion will still be the same.

4.5. Summary and general discussion

Table 12 summarises the suitability of the different implementation steps, and variations thereof, to respond to the potential drivers of the transformation of the cluster. In Table 12, an arbitrary and qualitative grey scale is defined, where black and white indicate the best-suited and worst-suited steps, respectively.

Under present market conditions, Implementation steps 1 and 2 (2b), which are mainly related to a change of feedstock, appear to be highly feasible from the economic point of view. Implementation step 3 requires a strong push to reduce CO_2 emissions, increase carbon recovery, and enable the possibility to balance the power network. Implementation step 4 can only be motivated if the cluster must absolutely achieve zero emissions of CO_2 to the atmosphere and/or 100% carbon recovery.

For Implementation steps 2b, 3b and 4b, only 2b can be justified in a business-as-usual scenario. Implementation steps 3b using biomass as fuel to the combustor can be motivated if there are strong initiatives to reduce fossil-CO_2 emissions, to increase the recycling rate of plastics,

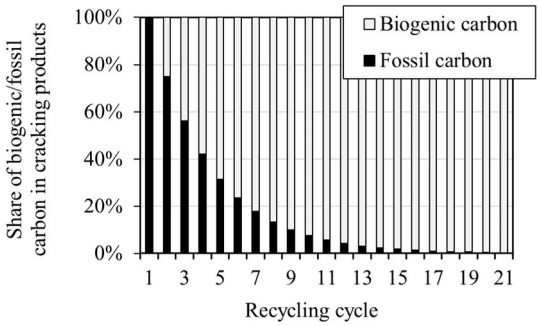

Fig. 16. Share of biogenic carbon in the cracker products after each recycling cycle in Implementation step 4b. The share of feedstock of Group *Biomass* in the input to the cracker is 25% (on a carbon basis).

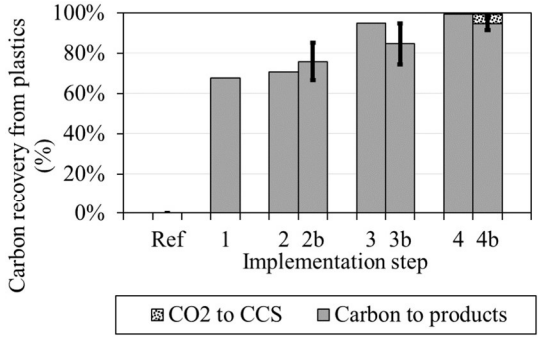

Fig. 18. Percentages of carbon from the plastic feedstock that are recovered in products in the different implementation steps. In Implementation steps 2b, 3b and 4b, the upper and lower boundaries of the error bars indicate the cases in which the fuel to the combustor is *Biomass* and plastic waste of Group 0, respectively.

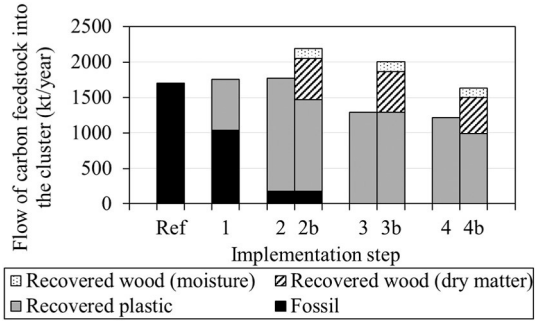

Fig. 19. Flows of carbon feedstocks and fuels into the clusters in the Reference case and in Implementation steps 1, 2, 3, and 4, as well as in the alternative cases with biomass fed to the combustor. Assumed fuel to the combustor in Implementation steps 2b, 3b and 4b: recovered wood with 20% moisture.

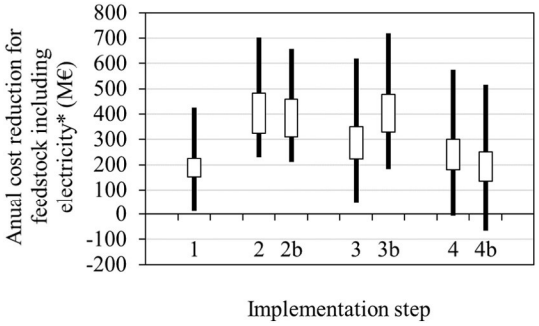

Fig. 21. Annual reduction of the cost for feedstock relative to the reference plant, with the reference costs of electricity and imported ethylene removed from the respective cases. White bars: range of best guesses. Black bars: expected maximum and minimum values. Prices and assumptions according to Tables 9 and 10, respectively. * Including only the additional electricity compared to that required in the reference case.

and/or to increase the share of biogenic carbon in the final plastic products. The latter will be a driver for Implementation steps 2b and 3b only if: the renewable carbon is allocated to the products despite the fact that all the renewable carbon atoms will be released as CO_2 to the atmosphere; or the biomass is fed to the cracker despite the thermodynamic penalty of choosing Route A/B instead of combustion Route C. Implementation step 4b is very unlikely from an economic point of view due to the high level of investment required, and other drivers need to be in place to motivate such investment. For example, in Implementation step 4b, the cluster would contribute to net removal of CO_2 from the atmosphere (Fig. 15), while greening the plastic stock (Fig. 16) independently of the method used for allocating the biogenic carbon, which is dictated by future regulations, and contributing to balancing the electrical power system, which, however, demands the installation of an ASU.

Regarding the overall contribution of the process to the circular use of plastic materials, the example of the cracking process presented here shows how 100% recycling into olefins can be achieved with PW of Group 2 in combination with PW of Group 0 and/or feedstocks of the Group *Biomass*. The example was applied to PE, which is a major component of packaging plastic and constitutes a vast and problematic type of waste in our oceans. If such a plastic stock was to be gathered from the oceans, a pre-washing step would be needed to reduce the salt content of the plastics before entering the crackers. Water from the drying of biomass in Implementation steps 2b, 3b and 4b could be used for this purpose, which in the current system can provide 130–145 kt/year of water (Fig. 19). Assuming water consumption of 2–3 m^3/t of plastic [11], the cracking plant has the capability to take in 40–70 kt/year of plastics from the ocean, while pre-washing them on-site without any requirement for additional fresh water. This flow of plastics represents 4%–7% of the total input of PW to the cracker in Implementation step 4b and a relatively small share (<1%) of the estimated mass of plastics entering our oceans annual (i.e., 4800–12,700 kt/year [4]). However, the major contribution of the thermal recycling route is that it can create a global price for the waste, thereby providing the economic driving force for the collection of plastics in all parts of the world, as well as an incentive to prevent their disposal in the oceans.

The thermal recycling proposed here is not limited to the PW of Group 2, as any sorted or mixed waste-stream, e.g., PW of Group 1, Group 0 or Group *Biomass* can be treated in similar systems. Fig. 24 summarises how the results presented here may be extended to other common PW streams, where specific units can be added to treat specific relatively homogeneous streams of PW of Group 1. For instance, pyrolysis at 300–600 °C is one option for materials that can be either decomposed into their monomers with high yields, e.g., PS and PMMA [42], or yield a relatively high-quality pyrolysis oil for further cracking, e.g., the BP approach for PVC and resins [27].

The additional units can be placed adjacent to the cracking plant or they can be decentralised. The advantage of centralising the production around the crackers is that it opens the possibility for heat integration and internal utilisation of waste streams within the processes, which, in turn, facilitate 100% recovery of materials and high energy efficiency. Processes that require heat, such as pyrolysis, can be centralised around the fluidised bed combustion unit, wherefrom the heat can be provided by diverting part of the hot bed material flow (heat carrier) into different reactors before the bed material returns to the combustor. The capacity of the combustor needs to be designed so as to cover the heat demand of the inter-connected processes. The controlled withdrawal of bed material from the combustor into adjacent reactors can be

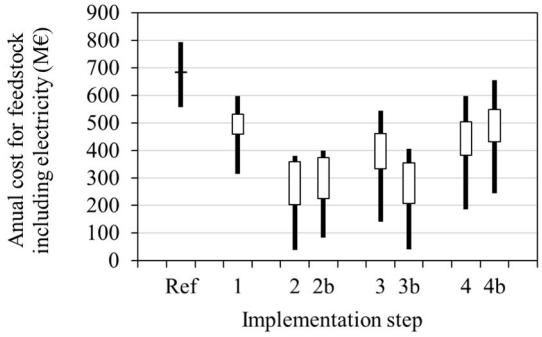

Fig. 20. Total annual costs for feedstock, biomass (in Implementation steps 2b, 3b and 4b), and electricity in the reference case (Ref) and in each implementation step. White bars: range of best guesses. Black bars: expected maximum and minimum values. Prices and assumptions according to Tables 9 and 10, respectively.

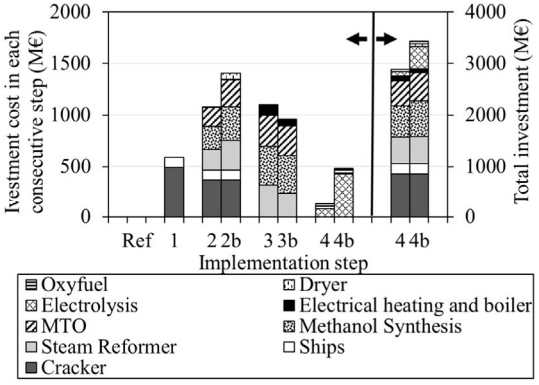

Fig. 22. Incremental investment cost of the proposed implementation steps, together with the final cost after Implementation step 4.

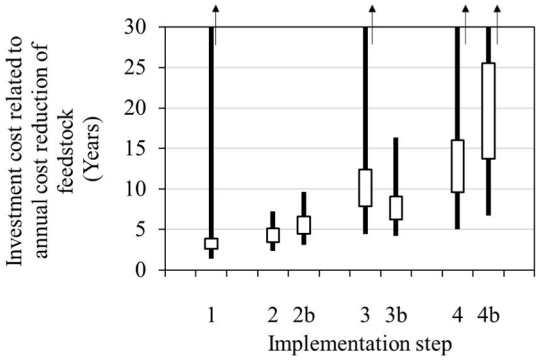

Fig. 23. Accumulated investment cost divided by the annual cost reduction of feedstock, including electricity, i.e., the "Payback time excluding financial costs". Payback times of >30 years are indicated by arrows. White bars: range of best guesses. Black bars: expected maximum and minimum values. Prices and assumptions according to Tables 9 and 10, respectively.

achieved using a mechanical solids valve, such as that developed by Lurgi to divert the flow of solids to an external heat exchanger in their CFB boilers with a fully refracted combustor [102], a system that is now sold by Doosan Lentjes [103].

Another aspect to take into consideration when recycling plastics of Group 1 and Group 0 is how to treat hetero-atoms present in the monomer structure, such as oxygen, chloride, sulphur and nitrogen, to avoid operational problems and/or to enable their recovery. During thermal conversion, these elements will be converted into stable products, such as CO_2, HCl, H_2S and NH_3, respectively, under tailored operating conditions [61,78]. While CO_2 can be separated in the down-stream gas separation unit, smaller amounts of HCl can be controlled effectively by the addition of sorbents that are based on lime, as demonstrated by Kaminsky's group [45]. A high content of chlorine is not expected nowadays in the PW, due to the limited share of PVC in mixed PW [10]. If PVC is present in substantial quantities, it can be separated quite easily due to its specific gravity being about 1.4. If such advanced sorting is done, PVC can be applied as the feedstock for the recovery of HCl. This could be achieved either through a pre-treatment step, if the remaining hydrocarbons are of interest as fuel, or through the AkzoNobel process [27,53]. When there are mixtures of nitrogen and chlorine in the PW, HCl and NH_3 are preferably separated as ammoniochloride in the filtration unit at the exit of the fluidised bed cracking unit, as the amount of PVC exceeds the amount of polyamide, NH_3. This phenomenon has been exploited in the Texaco process [27].

Furthermore, the process should handle the streams of additives that accompany the PW, including fillers, carbon fibres, and carbon black, so they do not accumulate in the system. Fillers are recovered in the filtration units as a blend of different types and are, consequently, of relatively low quality. For instance, the recovered calcium carbonate fillers will most likely not be of sufficient quality to be re-used as fillers in new plastics, so alternative uses should be considered, e.g., as a filling material in construction. In the cases of carbon black and carbon fibres, they will undoubtedly be converted to CO_2 once they move through the combustion side of the DFB. The recovery of carbon in the form of fibres is challenging, as the feedstock preparation degrades the composite into small pieces. Nevertheless, the cracker can provide the building blocks to produce new carbon fibres, e.g., propylene and ammonia for the SOHIO acrylonitrile process [104]. Carbon black, in contrast, can be recovered by pyrolysis if there is an interest in doing so, e.g., through the pyrolysis of tyres by Enviro in Sweden [105], or it can be produced from hydrocarbon fractions of low economic value via a plasma or electric arc reactor. In the latter system, fractions that have a high aromatic content can be converted into carbon and hydrogen [106]. If the hydrogen-to carbon ratio of the feed is appropriate, the electric arc furnaces would also be suitable for the production of acetylene and ethylene, assuming that the price of electricity is low [107]. The implementation of these additional processes will depend on the market price not only of the final product, but also on that of handling mixed PW.

5. Conclusions

The energy and carbon balances, together with the economic assessment related to the step-wise transformation of an existing

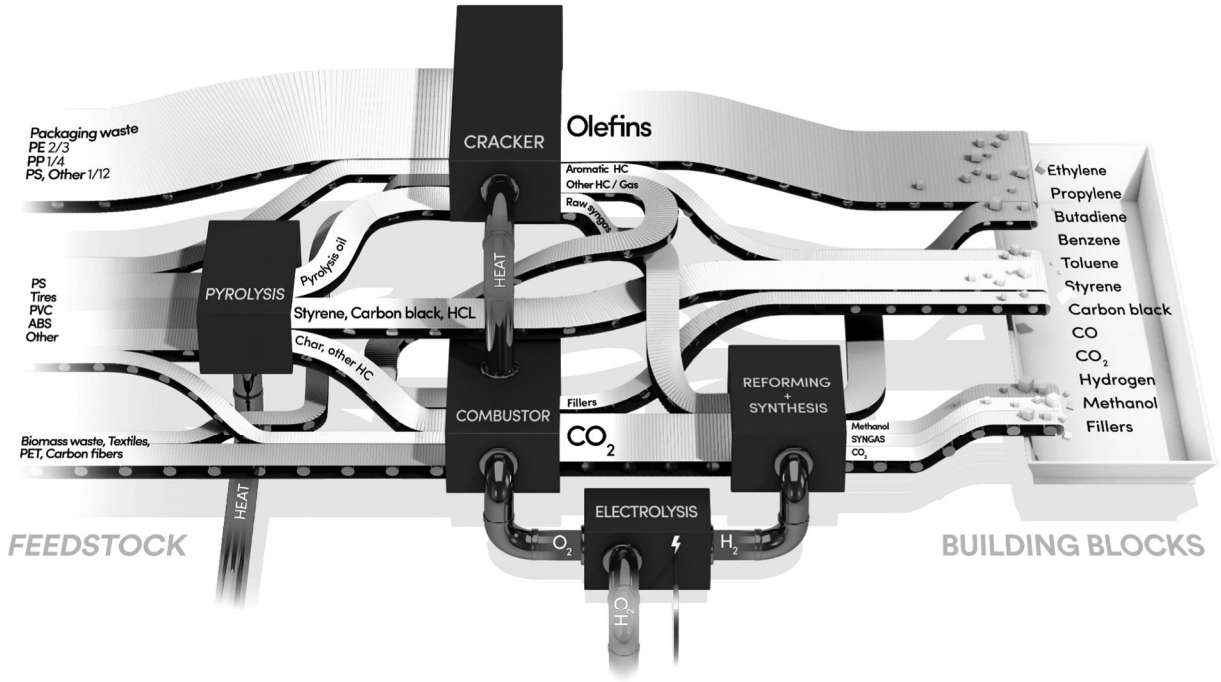

Fig. 24. Schematic of a technical solution for closing the material cycle of plastics using thermochemical recycling, which can handle any type of plastic waste (sorted or mixed) with close to 100% carbon recovery.

Table 12
Suitabilities of the different implementation steps to respond to the different drivers for the transformation of the cluster. Grey-scale, where black and white indicate the best-suited and worst-suited implementation steps. *Oxy* refers to oxy-combustion supported by an ASU.

	Implementation step															
	1	2	2 oxy	2b		2b oxy		3	3 oxy	3b		3b oxy		4	4b	
Priority				*Biomass*	Group 0	*Biomass*	Group 0			*Biomass*	Group 0	*Biomass*	Group 0		*Biomass*	Group 0
Business as usual																
Increase carbon recovery from plastics																
Reduction of fossil-CO_2 from site																
Increase the share of biogenic carbon in the plastics - allocation to mass balance cluster																
Increase the share of biogenic carbon in the plastics - strict allocation over each process unit				**		**				**		**				
Maximise the use of intermittent sources in the power sector															*	*

*ASU required to allow balancing of the power system.
**If biomass is fed to the cracker instead of to the combustor.

petrochemical cluster into a thermochemical recycling plant for 100% recovery of plastics reveal that:

- The penalty incurred by the transformation in terms of energy efficiency is limited to a few percentage points, being <10% for all the implementation steps.
- The environmental benefits of the transformation are highly dependent upon how the performance of the cluster is assessed and which allocation rules are applied. This is especially important when biomass is introduced into the cluster.
- From the economic perspective, switching the feedstock from the present (based on virgin fossil fuels) to re-circulated plastics is warranted.
- To achieve the goal of 100% recycling of plastics into monomers via cracking requires stronger pressure from Society, including economic incentives, valorisation of the net extraction of CO_2 from the atmosphere and/or valuing the possibility to contribute to balancing the electrical power network.

Overall, the transformation of an existing cluster that takes advantage of the existing infrastructure is technically feasible and there are possibilities to use any type of plastic feedstock (mixed or sorted) in a circular way. However, the economic feasibility of full transformation of the petrochemical cluster with 100% carbon recycling will depend on the regulatory framework in place.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

Funding for this project was provided by the Swedish Energy Agency through the project *Innovative Conversion Processes* at the Chalmers Power Center (2013-007387) and the *Material recovery from plastic fractions* via *thermal conversion* project (2017-001980). Additional funding was from the Swedish Gasification Center (SFC) through a Swedish Energy Agency grant (2016-011824).

The authors thank Jan Kjärstad for his contributions with cost data, and Måns Collin, Lars Josefsson, and Anders Gustafsson for valuable comments on the manuscript.

Appendix 1. Carbon balances

Carbon balances of the cluster in each implementation step. The thickness of each arrow is proportional to the annual mass flow of carbon in each respective stream (kt C).

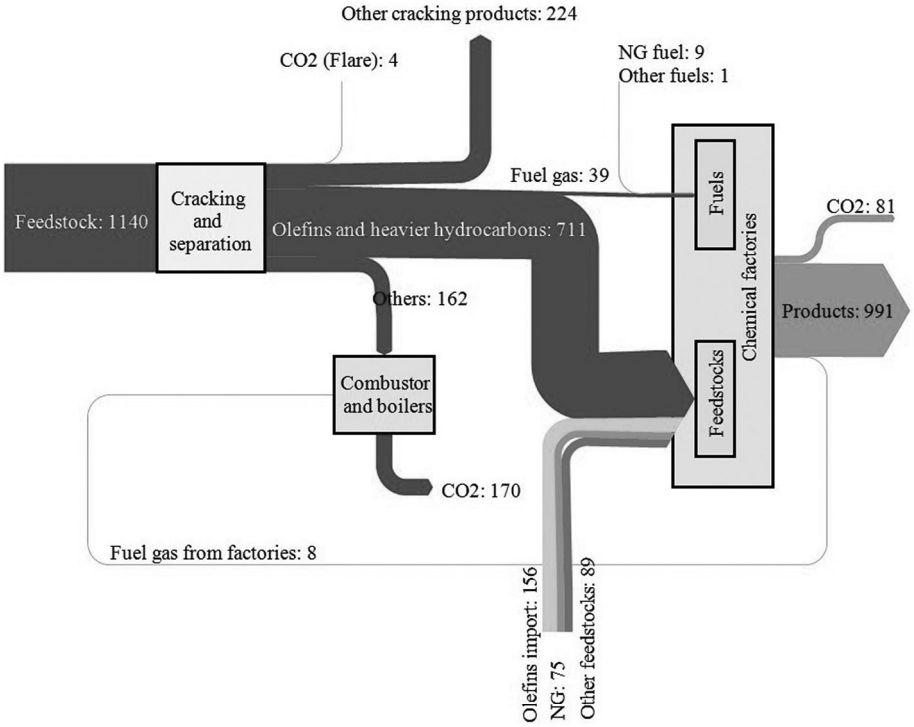

Fig. A1.1. Carbon balance in the Reference case. Other products include fuel oil and other hydrocarbons >C_5.

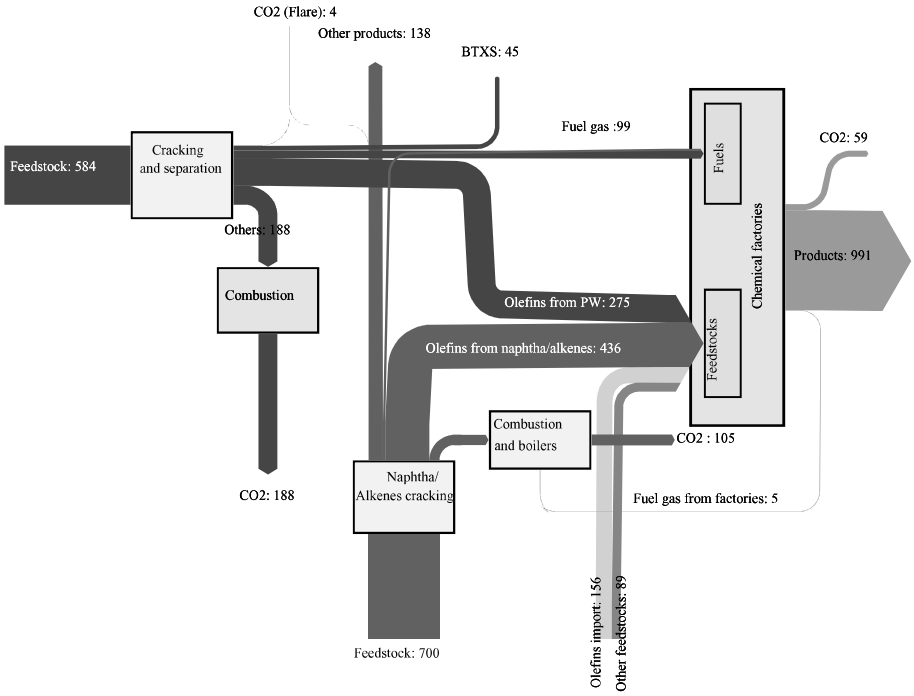

Fig. A1.2. Carbon balance in Implementation step 1 (kt C). Red: Flows related to the cracking of naphtha/alkenes. Dark blue: Flows related to the cracking of plastic wastes. The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and the fractioning and recovery sections. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

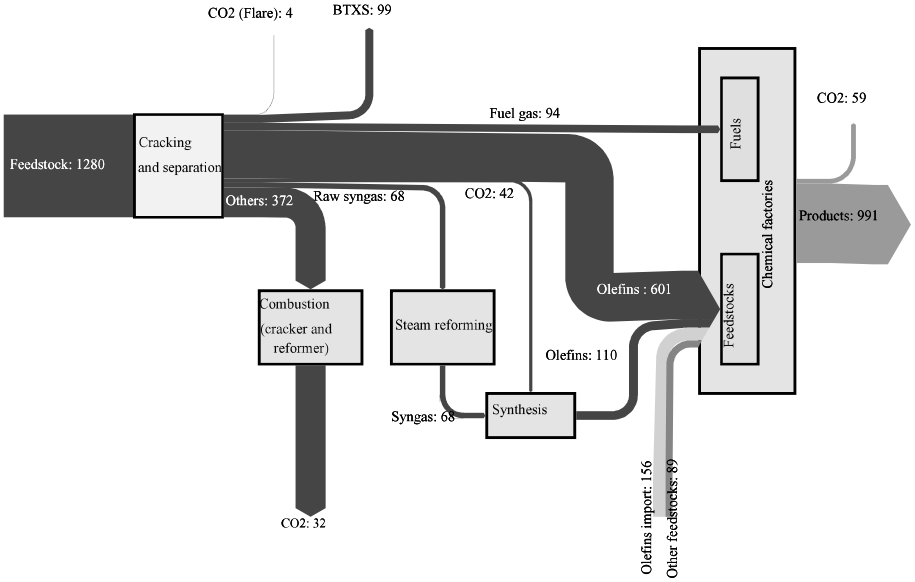

Fig. A1.3. Carbon balance in Implementation step 2 (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, fractioning and recovery sections.

and recovery sections.

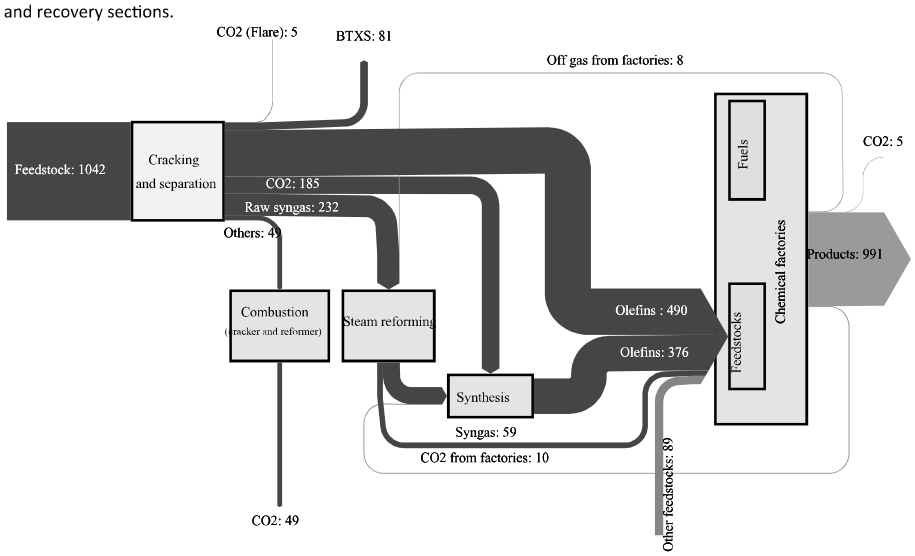

Fig. A1.4. Carbon balance in Implementation step 3 (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and fractioning and recovery sections.

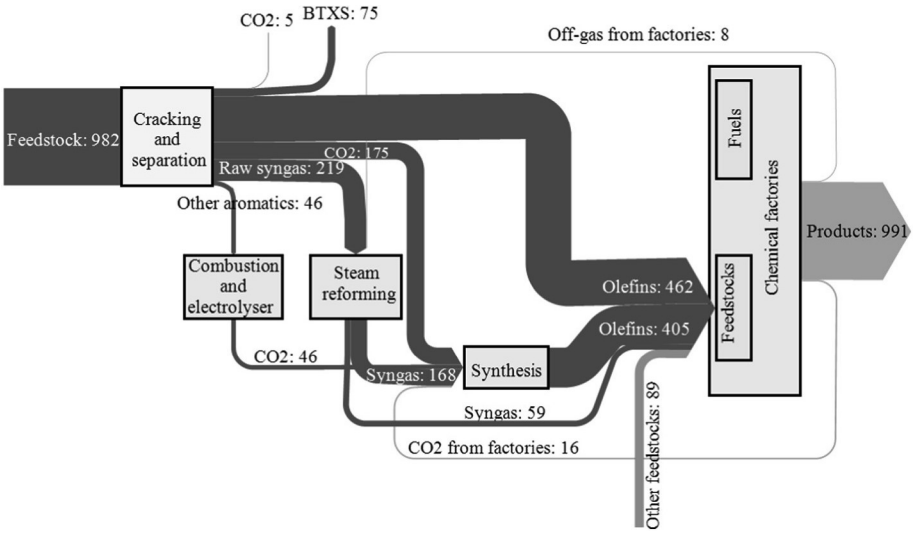

Fig. A1.5. Carbon balance in Implementation step 4 (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and fractioning and recovery sections.

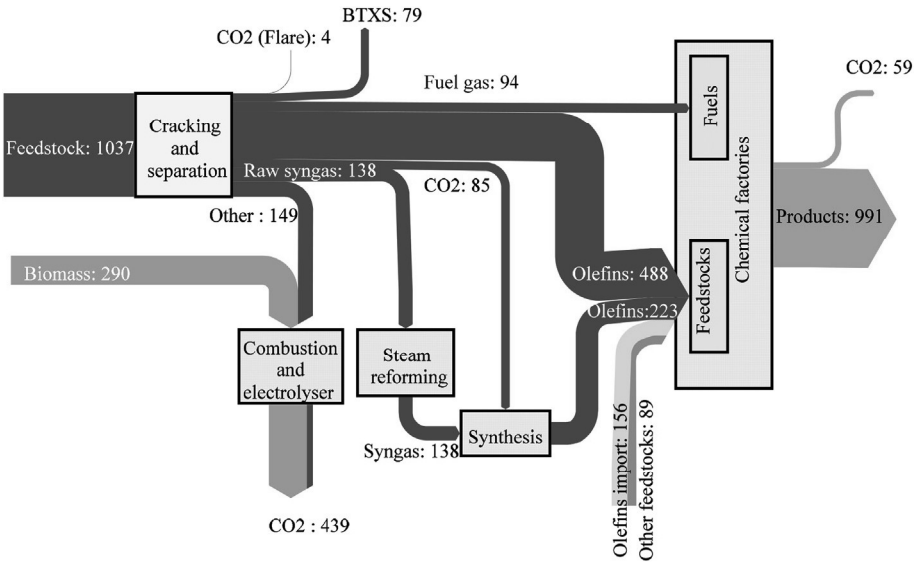

Fig. A1.6. Carbon balance in Implementation step 2b (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and fractioning and recovery sections. Green arrows, Biogenic carbon; Dark-blue arrows: carbon derived from plastic wastes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

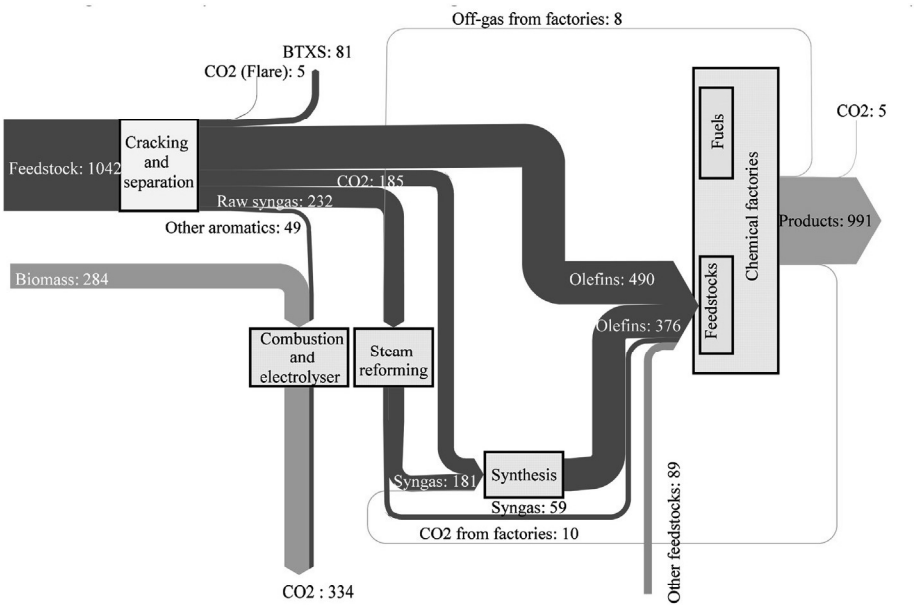

Fig. A1.7. Carbon balance in Implementation step 3b (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and fractioning and recovery sections. Green arrows, Biogenic carbon; Dark-blue arrows: carbon derived from plastic wastes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

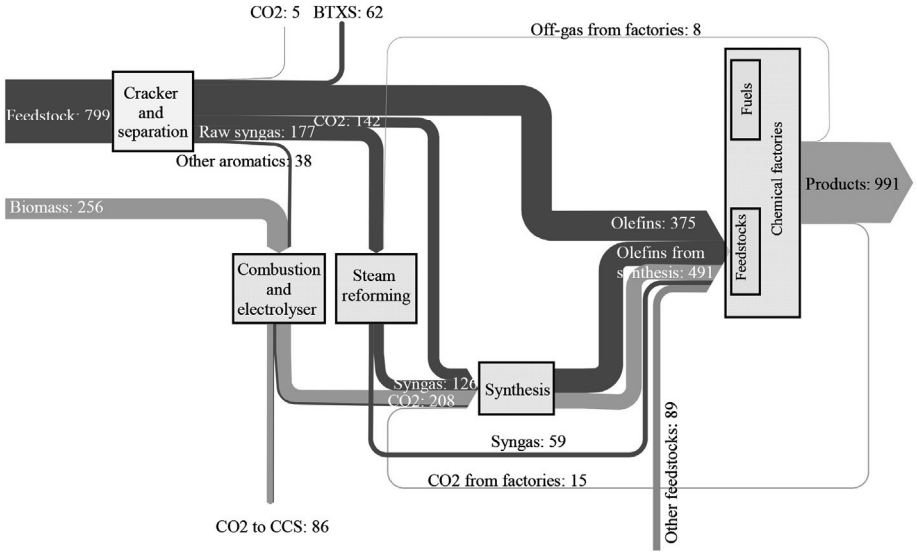

Fig. A1.8. Carbon balance in Implementation step 4b (kt C). The item *Cracker and separation* includes the cracking reactors, first cleaning steps, and fractioning and recovery sections. Green arrows, Biogenic carbon; Dark-blue arrows: carbon derived from plastic wastes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Appendix 2. Energy balances

Energy balances of the cluster in each implementation step. The thickness of each arrow is proportional to the annual energy flow in each respective stream (GWh).

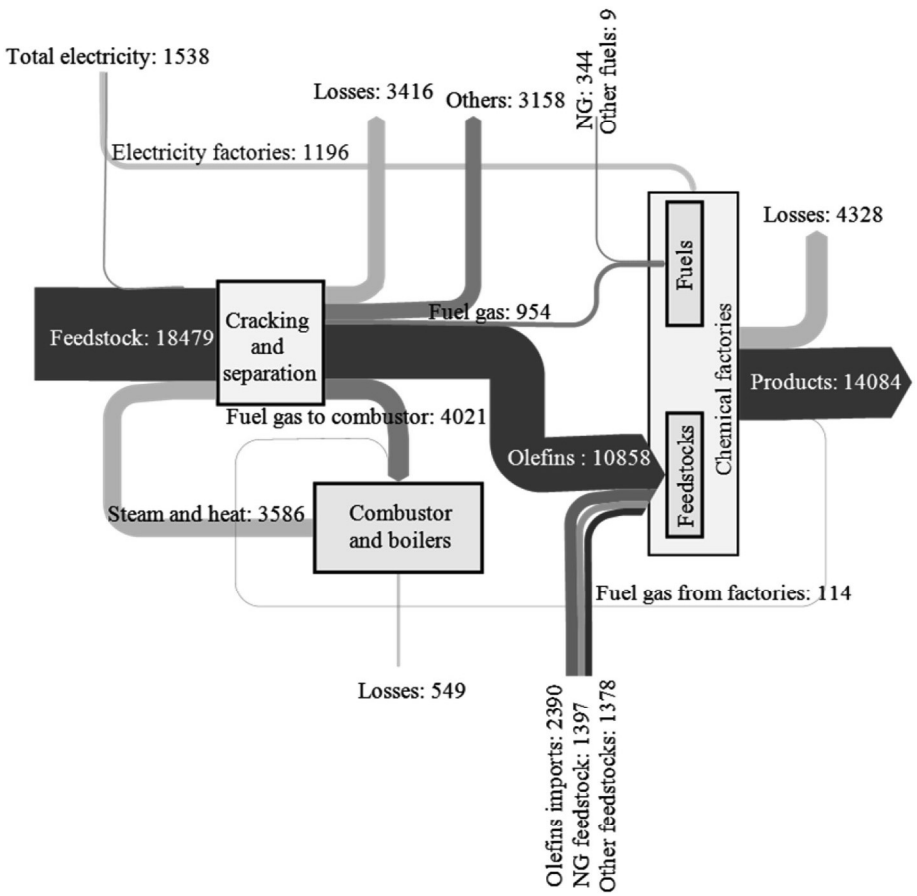

Fig. A2.1. Energy balance (GWh) in the Reference case.

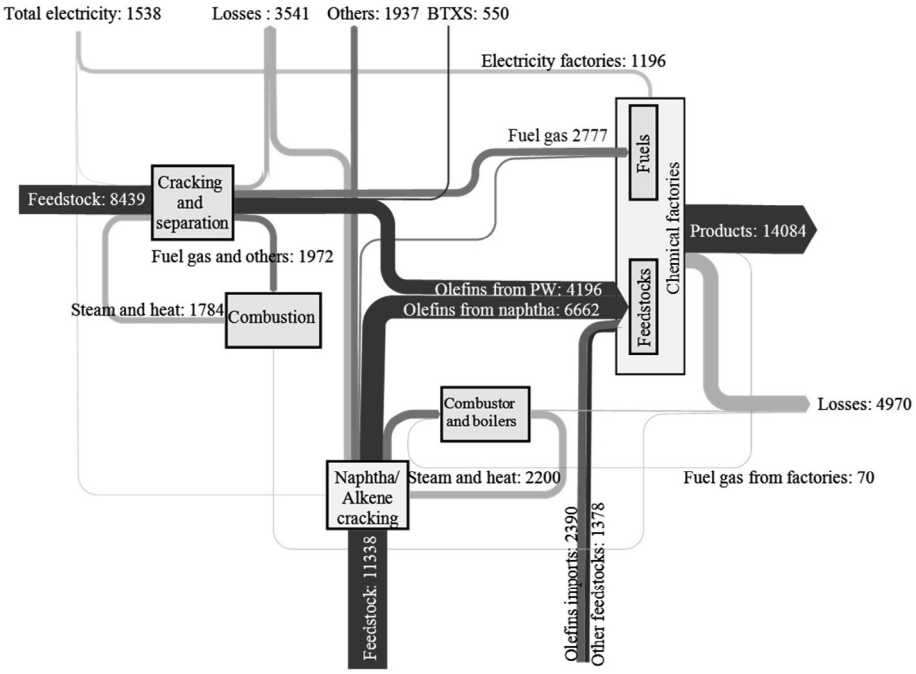

Fig. A2.2. Energy balance (GWh) in Implementation step 1.

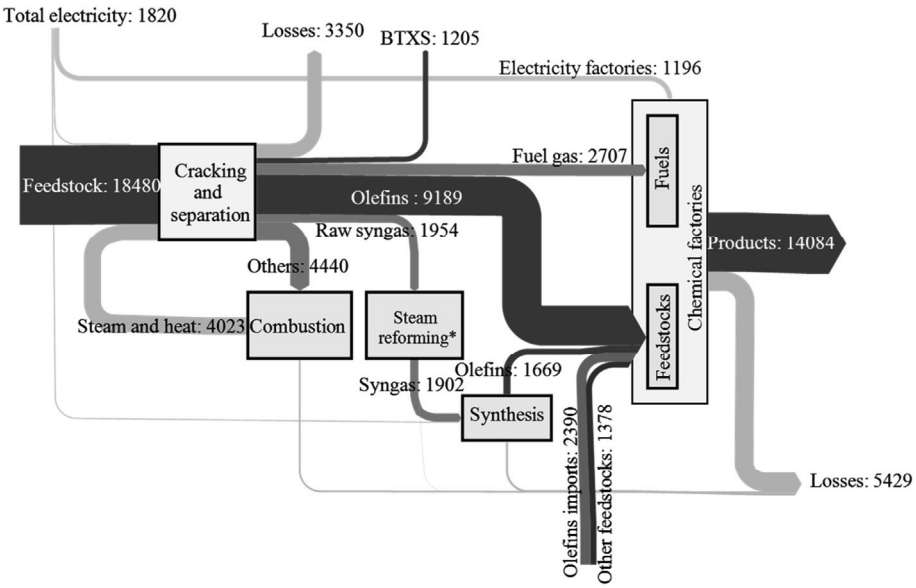

Fig. A2.3. Energy balance (GWh) in Implementation step 2. *Heat demand accounted for in the *Combustion* box. Heat losses are related exclusively to the chemical reactions.

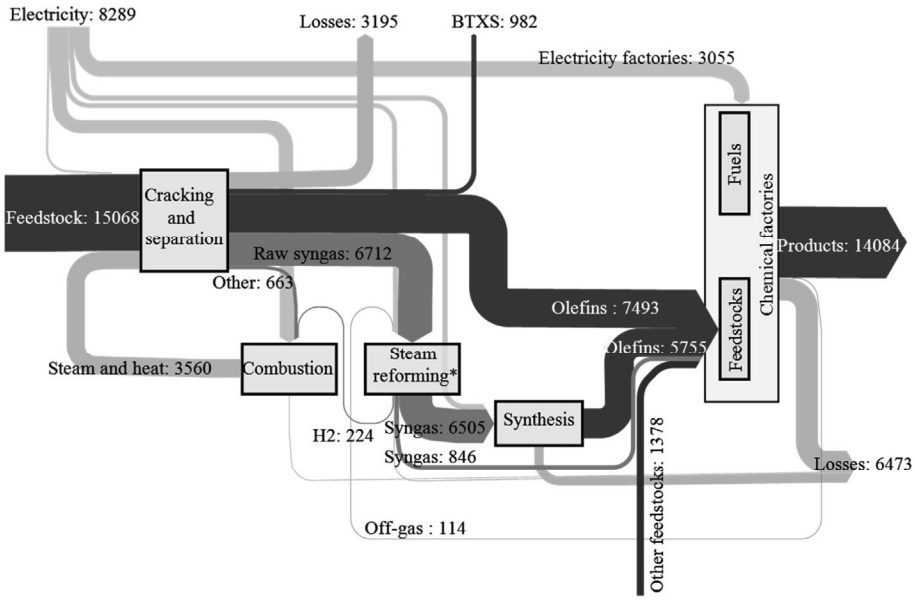

Fig. A2.4. Energy balance (GWh) in Implementation step 3. *Heat demand accounted for in the *Combustion* box. Heat losses are related exclusively to the chemical reactions.

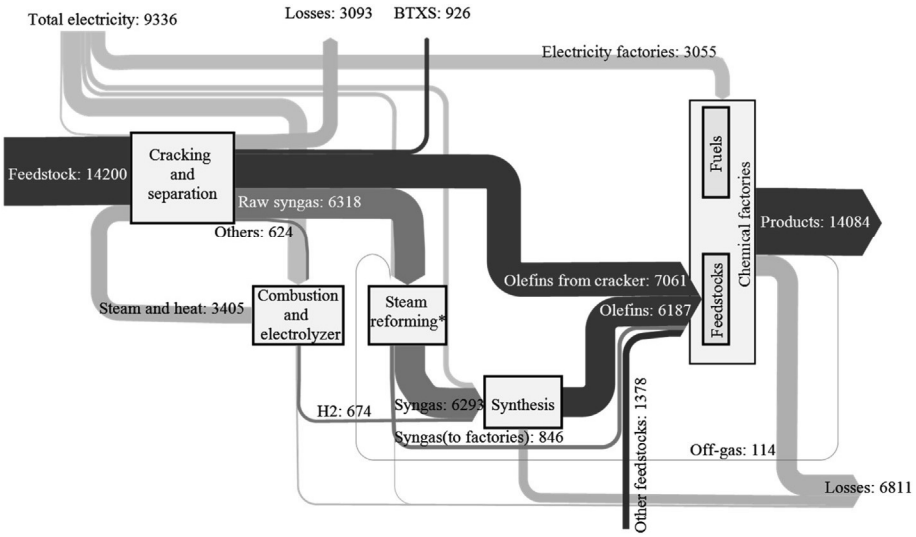

Fig. A2.5. Energy balance (GWh) in Implementation step 4. *Heat demand accounted for in the "Combustion" box. Heat losses are related exclusively to the chemical reactions.

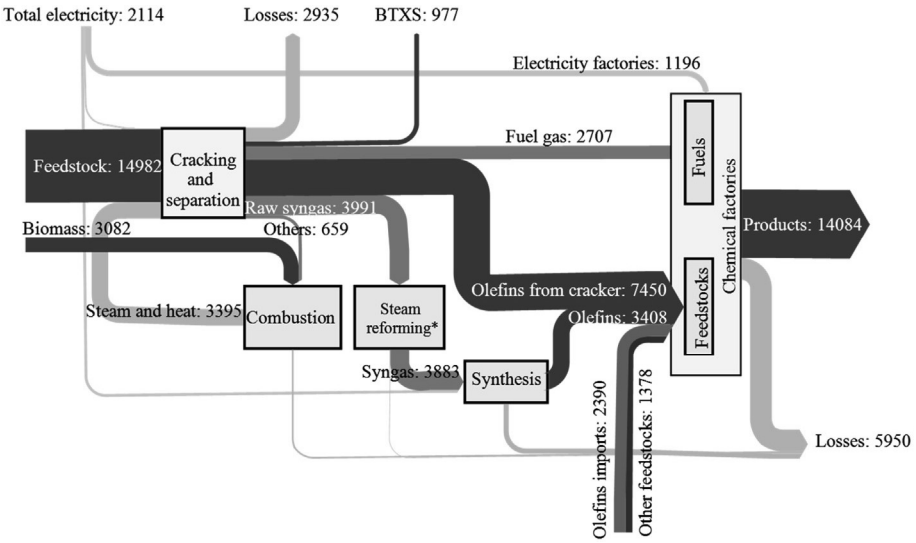

Fig. A2.6. Energy balance (GWh) in Implementation step 2b. *Heat demand accounted for in the *Combustion* box. Heat losses are related exclusively to the chemical reactions.

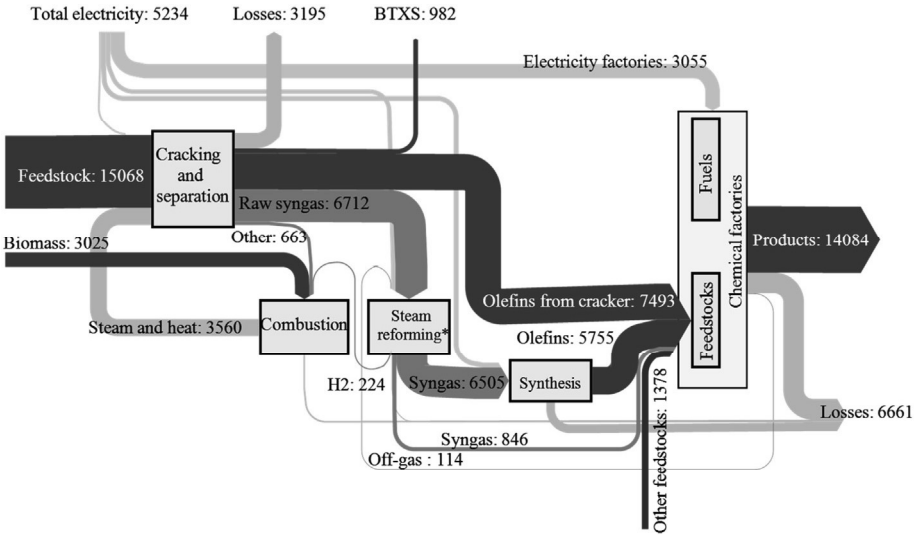

Fig. A2.7. Energy balance (GWh) in Implementation step 3b. *Heat demand accounted for in the *Combustion* box. Heat losses are related exclusively to the chemical reactions.

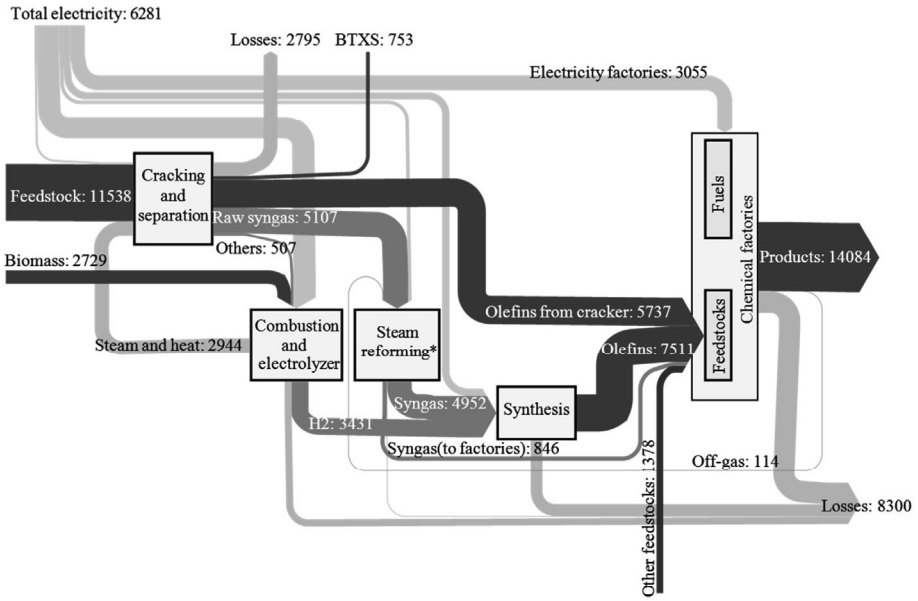

Fig. A2.8. Energy balance (GWh) in Implementation step 4b. *Heat demand accounted for in the *Combustion* box. Heat losses are related exclusively to the chemical reactions.

Appendix 3. Installed capacity in each implementation step

Table A3.1
Additional installed capacity from previous implementation step.

	Implementation step				Unit
	1	2	3	4	
Cracker[a]	993	1181	0	0	MW
Ships[b]	200	200	0	0	kt PW
Steam reformer	0	230	573	0	MW
Methanol synthesis	0	291	788	0	kt/year methanol
MTO	0	191	518	0	MW
Electrical heating	0	33	551	0	MW
Electrical boiler	0	0	219	0	MW
Electrolysis	0	0	0	106	MW
Dryer	0	0	0	0	MW
Oxy-combustion[c]	0	0	0	1	unit

[a] One cracker has a capacity of 393 MW; total of seven crackers by step 2.
[b] Each ship has a capacity of 50 kt; total of eight ships by step 2.
[c] Arbitrarily assumed that the carbon recovery system in connection to the application of oxy-combustion is limited to 50 M€.

Table A3.2
Additional installed capacity from previous implementation step. Route Implementation steps 2b, 3b and 4b.

	Implementation step				Unit
	1	2b	3b	4b	
Cracker[a]	993	1132	0	0	MW
Ships[b]	200	200	0	0	kt PW
Steam reformer	0	470	334	0	MW
Methanol synthesis	0	595	715	0	kt/year methanol
MTO	0	391	470	0	MW
Electrical heating	0	68	196	0	MW
Electrical boiler	0	0	219	0	MW
Electrolysis	0	0	0	538	MW
Dryer	0	580	0	0	MW biomass
Oxy-combustion[c]	0	0	0	1	unit

[a] One cracker has a capacity of 393 MW.
[b] Each ship has a capacity of 50 kt.
[c] Arbitrarily assumed that the carbon recovery system in connection to the application of oxy-combustion is limited to 50 M€.

Appendix 4. Input data used for the calculations

Chemical factory	Value	Unit	Assumptions used in calculations
Olefin	1011	Ton/year	
Syngas H2/CO ratio of 1.4	59	Ton/year	Assumed that all ingoing gases shift to CO and H2 before methanol synthesis in order to give a moderate estimate of energy consumption of the process and energy needed are provided by the electricity
Other import hydrocarbons	7420	$x10^6$ mol C/year	
	1378	GWh/year	
Electrical demand	1196	GWh/year	
Heat demand	1859	GWh/year	Assumed equal to heat from combustion processes in the factories, no efficiency gain is allocated to the electrification
Off gas	645	$x10^6$ mol C/year	Burned to cover heat demand in implementation steps 1 and 2, sent to a steam cracker in step 3 and 4
	114	GWh/year	
Fractionation	$[] = []_{ref}^{*} (m_{olefins}/m_{olfins\_ref})$		Energy demand normalized to olefins produced in cracker
Electricity demand references	342	GWh/year	Also included the electricity to cracker
Steam demand references	1049	GWh/year	
Flare	398	$x10^6$ mol C/year	In the calculation extracted from the CH4/CO/H2 entering the fractionation
Cracker			
Inlet temperature	20	°C	
Steam to carbon in the feedstock	0.5	mol_{H2O}/mol_C	On mass, this corresponds to steam to feedstock ratio of 0.64
Outlet temperature	825	°C	
Air to fuel ratio combustion	1.2		
Flue gas temperature	150	°C	
Heat losses through reactor walls	3%		Related to heat demand of cracker process
Steam reformer			Assuming reaction reach equilibrium
Pressure	100	kPa	
Temperature	827	°C	
Steam to methane ratio	1.5	mol_{H2O}/mol_{CH4}	
Heat loss, related to the heat of reaction	25%		Combustion side of the process integrated with combustion side of the cracker
Methanol synthesis @ 128 bars			
Compression 1 to 128 bars	1.75	MJ/nm^3	
Conversion of syngas to methanol			Recirculation within the cluster gives in the calculation a net yield of carbon into the synthesis to methanol of 100%, where the loss of carbon is in the calculation through the flare in the fractionation step
Heat of reaction			Is partly providing heat to MTO process if integrated otherwise regarded as a heat loss
MTO process @ 1 bar			
Conversion of methanol to olefins			The temperature of the process gives mainly the ratio between ethylene and propylene, as well as conversion yield of methanol, which in the calculation is recovered within the MTO process or via the cracker, carbon lost in the overall process is via the flare in connected to the fractionation. In the calculation, the mix of ethylene and

(*continued*)

Chemical factory	Value	Unit	Assumptions used in calculations
			propylene is regarded as ethylene in order to not underestimate heat of reaction
The ingoing concentration of methanol	1	Based on moles	
Inlet temperature	20	°C	
Outlet temperature	420	°C	
Heat loss, related to the heat of reaction	25%		
Electrolyser			
Efficiency based on the lower heating value	75%		

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